Appendix I
Shell for Analytical Chemistry Requirements

I.1   Purpose and Use

The policy of the U.S. Army Corps of Engineers (USACE) is to produce data of known quality that meet all project-specific requirements established by the Technical Project Planning Team as outlined in EM 200-1-2. In order to meet those goals, ER 1110-1-263 requires that all analytical service providers have verifiable quality systems compliant with the principles of Guide 25 of the International Organization for Standardization/International Electrotechnical Commission (ISO/IEC) (1990). Many of the components specified within this appendix are pursuant to those standards. However, refer to EM 200-1-1 for comprehensive guidance on the requirements needed to comply with this directive. In general, Sections I.1 through I.3 are for use by personnel generating the contract Scope of Work (SOW) or project Sampling and Analysis Plan (SAP), providing guidance on the establishment of project measurement quality objectives based upon the intended use of the data; and Sections I.4 - I.13 are for the analytical service providers or laboratory, providing guidance on implementation and interpretation of the policy and method requirements established herein. In addition, bold-face italicized type is utilized throughout the guidance to cue input based upon project-specific requirements, to clarify USACE project policy, or to identify when appropriate notification procedures to the client/data user are required. To support the application of this guidance to a project, it has been designed to allow a project team/chemist to apply the guidance as a whole or inappropriate sections by reference within a contract or SOW, using the laboratory measurement quality objectives as specified, or modify them (make them more or less stringent) based upon project requirements. USACE technical personnel should also review topics in bold-face type within applicable analytical sections to identify necessary project-specific information. These project-specific clarifications should then be discussed or summarized within the project documents (e.g., SOW and SAP) to avoid misunderstandings between the laboratory and USACE. Items included as recommendations also have the potential for enforcement as a requirement based upon project data quality objectives (DQOs). Summary tables are included within this guidance to outline the specific quality control (QC) items for each method and associated measurement quality objectives. This summary format is designed to facilitate the adjustment of QC parameters to reflect project-specific DQOs. It should be noted that these measurement quality objectives apply to the laboratory QC procedures exclusively, and do not address the field control sample QC requirements. The calculation of data quality indicators (DQIs) for laboratory precision and bias represents only the analytical error or an estimated 20 percent of the total error associated with each sample. For guidance on establishing field (quality assurance (QA)/QC) replicate precision requirements, refer to EM 200-1-6 and Grant, Jenkins, and Mudambi (1996).

I.1.1   USACE data needs.

I.1.1.1   USACE currently executes restoration activities under several environmental regulatory programs. The analytical testing of various environmental samples is often a significant part of these activities. The data must be produced by a process or system of known quality to withstand scientific and legal challenge relative to its intended purpose. To give the USACE programs the greatest flexibility in the execution of its projects, the SW-846 methods (U.S. Environmental Protection Agency (USEPA) are generally the methods employed for the analytical testing of environmental samples. The decision to focus on SW-846 methods is due largely to their being comprehensive for various media and chemical parameters; subsequent promulgation of method updates keeping methods current with instrument capabilities and industry standards; and their flexibility allowing adaptation to individual project-specific requirements. When SW-846 or other national standard methods are not available for the medium, methods published by reputable technical organizations (e.g., American Society for Testing and Materials (ASTM)) or refereed scientific journals should be pursued. The use of nonstandard methods shall be subject to agreement between

the laboratory and USACE. All nonstandard methods shall be fully documented within project-specific SAPs, and must undergo full review and approval procedures as outlined in the SAP.

I.1.1.2   The Shell for Analytical Chemistry Requirements establishes a basic approach for application of analytical chemistry methods (e.g., SW-846, performance-based methods) by the USACE.   The concepts included here specify a baseline implementation of several analytical chemistry methods. However, when a performance-based analytical approach is employed, additional regulatory approval may be necessary to ensure acceptance of data generated.

I.1.2   Project chemical data quality management (CDQM).

I.1.2.1   All Hazardous, Toxic, and Radioactive Waste (HTRW) projects require a comprehensive program of CDQM activities to support the generation of data of acceptable quality. EM 200-1-6 outlines several QA techniques that may be applied to help evaluate the quality of sampling and analyses performed. USACE project team members must develop a project-specific CDQM program by defining appropriate monitoring techniques based upon the type of data generated and its intended purpose. The compliance monitoring techniques chosen for a project are then detailed within the project contracting documents (e.g., SOW, guide specification), if applicable. In general, data collection efforts involve the design of project plans to achieve the data quality objectives, which support progress toward site closeout; correct implementation of those project plans; and assessment of the data to determine if the data quality objectives were met. ***To ensure full accordance among the USACE, Architect-Engineer firms and laboratories, the project plans (i.e., SAP) shall discuss all of the project-specific compliance monitoring CDQM activities applied to the given project.*** For instance, compliance monitoring activities may include laboratory accreditation requirements; collection/analyses/evaluation of appropriate field and laboratory control samples; measurement quality objectives attainment/corrective action scenarios; external audits (field and/or laboratories); or external data assessment procedures (i.e., data validation, magnetic tape audits).

I.1.2.2   In order to promote flexibility as well as some degree of consistency in the data generated to support USACE HTRW projects, when inconsistent or mutually exclusive method requirements are encountered, the following hierarchy applies:

• Project-specific documents (e.g., SAP).

• USACE Engineer Manuals or other policy guidance.

• SW-846 methods.

Hence, the laboratory should be aware of and review these sources to determine project-specific DQOs and applicable project requirements.

I.1.3   Performance based methods implementation.

I.1.3.1   As the various Federal, State, and local regulatory agencies acknowledge the adoption of Performance Based Measurement Systems (PBMS) as a means to achieve required environmental monitoring, the applicability of performance-based methods to individual projects will increase. PBMS are defined by USEPA as a set of processes wherein the DQOs of a monitoring program are designated, rather than specifying the approved standard analytical method necessary. To date, however, the details for establishing data quality and performance requirements for required monitoring to support the assessment and selection of performance-based methods have not been fully defined within the various USEPA and State environmental offices. In addition, progress in updating Federal, State, and local regulations to incorporate

the PBMS philosophy and remove the requirements for specified standard reference methods for the use of new and innovative technologies is necessary to help assure successful PBMS implementation. Currently, PBMS has encouraged the application of field analytical technologies to environmental restoration projects.

I.1.3.2 This performance-based method approach empowers the analytical service (data) provider with the flexibility to vary aspects of an analytical system and protocols as long as the demonstrated method performance meets the requirements established by the data user(s). A PBMS may employ completely different chemistries or detection systems from those identified in current standard reference methods; may alter sample preparatory or determinative procedures that enhance or inhibit extraction/digestion or signal efficiency; or may encompass only minor modifications to a standard method instrument configuration. Due to this inherent flexibility, additional effort is necessary in the planning and executing phases to ensure successful implementation of performance-based methods. ***This may include any or all of the following: establishing and maintaining proper PBMS documentation (i.e., method standard operating procedures (SOPs), records of data analyses/results); USACE and regulatory agency review/approval; evaluation of method performance via DQIs; and comparison of PBMS data to data generated from a standard reference method.*** Before implementation of performance-based methods, the analytical service provider must establish the capabilities of the method/technique, to include selectivity, sensitivity, range of detection, precision, and bias. These are evaluated against performance criteria established by USEPA, State regulatory agencies, or the technical project planning team to assess the usability of the PBMS or performance-based method. ***The accuracy of the developers'/manufacturers' claims and technical data and the comparability amongst various techniques should be scrutinized for it is an area that is in the early stages of standardization by USEPA.*** In the event that the method capabilities do not meet project requirements, differences shall be reconciled prior to project execution. Reconciliation may require modifying the selected method, choosing an alternative method or techniques, or modifying the project DQOs. ***Project application of performance-based methods requires that performance be demonstrated for the analytes of concern, at the levels of concern in the matrix of concern within a specified acceptable error tolerance.*** Data generated from performance-based methods are evaluated using the same procedures as standard reference methods, as presented in Sections I-9, I-10, and I-11. In addition, if the PBMS is considered an emerging technology, lacks established records of use or application to environmental matrices, or varies significantly from the standard reference method, suggest acquiring a percentage of split samples for redundant analysis by the standard reference method. This will allow a comparison or calculation of a correlation factor between the data sets to evaluate the usability of the performance-based method in that project matrix.

I.2   SW-846 Methods Organization

I.2.1   SW-846 Methods implementation. EPA/SW-846 contains the analytical testing methods that the USEPA has evaluated and found to be acceptable for analysis of samples under Subtitle C of the Resource Conservation and Recovery Act (RCRA). As stated in the Final Rule that incorporated the Third Edition of SW-846 (and its updates) into the RCRA regulations, this publication is required to be used for only certain activities in the RCRA program. In other situations, this USEPA publication functions as a guidance document setting forth acceptable, although not required, methods to be implemented by the user, as appropriate, in satisfying RCRA-related sampling and analysis requirements. These methods are intended to promote precision, accuracy, low bias, sensitivity, specificity, and comparability of analyses and test results. SW-846 includes several separate test methods addressing hundreds of analytes. For any given analyte, multiple methods, with varying detection limits, are potentially available from this resource. As noted in Section I.1.1, USACE data needs focus on the use of SW-846 because the methods are comprehensive for many environmental matrices and chemical parameters, they are current with instrument capabilities and industry standards, and they are flexible to adaptation based on project-specific requirements.

I.2.2   SW-846 Method updates. SW-846 is a dynamic document that is subject to change as new information and data are developed. Advances in analytical instrumentation and techniques are continually reviewed by the USEPA Office of Solid Waste and Emergency Response and periodically incorporated into SW-846 updates to support changes in the regulatory program and to improve method performance. Any of these promulgated or draft SW-846 methods or other methods may be used by USACE to support the project-specific requirements. However, it should be noted that recent SW-846 updates have deleted several methods where technology was considered outdated (i.e., packed chromatographic columns) and incorporated several new field screening methods. Therefore, it is advisable to maintain current knowledge of these method advances and design projects, taking advantage of the most recently promulgated methods.

I.3   Project Objectives for Data Measurement

I.3.1   Data quality objectives (DQOs). To generate data that will meet the project-specific require-ments, it is necessary to define the types of decisions that will be made and to identify the purpose of the data. DQOs are an integrated set of specifications that define data quality requirements based on the intended use of the data. Project-specific DQOs are established to encompass both field and laboratory operations. The DQO process leads to the specification of the following at a minimum: sample handling procedures; preparatory (extraction/digestion), cleanup, and determinative methods; target analytes; method quantitation or reporting limits; field and laboratory quality control samples; measurement quality objectives (QC acceptance limits) for DQIs (formerly precision, accuracy, representativeness, comparability, and completeness (PARCCS) parameters); required corrective actions; and data assessment procedures necessary to meet the intended use of the data. Special considerations that may also apply include internal laboratory sample chain-of-custody, data confidentiality, data archival, or data retention requirements beyond those stated herein. In the generation of the SAP, whether this is done by contractor or USACE personnel, a number of steps must occur at the planning stages for each project phase by various technical disciplines to identify all necessary data needs to formulate the project DQOs that support the project through close-out. Each project phase will have different information requirements and therefore different data needs. However, the project strategy as a whole must be kept in mind to optimize each phase, streamlining the project whenever possible to avoid repetitive sampling and analytical work efforts. These planning exercises will then lead to a comprehensive sampling and analytical protocol for each phase. These tasks may be performed by USACE for work done in-house, prescribed for a contractor within a Scope of Work, or developed by the contractor directly into the SAP. Refer to EM 200-1-2 for information on the development of these goals and objectives for data collection design.

I.3.1.1 Assessment of data needs. As presented in EM 200-1-2, data needs are determined for the project based upon the decisions that need to be made. At the same time, a determination of the data quality required for each piece of data (data need) must also be defined by the eventual data user. This information, routinely expressed as an uncertainty allowed or a qualitative statement of requirements, will help other technical planners (data implementors) to identify applicable sampling and analytical protocols to generate the required data. The data needs quality requirements are assessed by analytical parameter (per matrix, per area). Since it is possible to have more than one data user requesting the same data need(s), the most stringent data user requirements are applied to ensure the suitability of these data by all requesting parties. This infor-mation is then used to decide an appropriate analytical strategy to generating the required data. The analytical strategy may use a combination of screening and/or definitive data to support field and project decisions.

I.3.1.2 Assessment of data collection options. Initially, the applicability of field analytical methods to the objectives of the project should be investigated. The rapid or real-time results help support field decisions to guide or direct sampling and analytical activities. Thereby streamlining progress toward site end goals. Field analytical methods include qualitative or semiquantitative field screening techniques (e.g., photoionization detector/flame ionization detector, immunoassay, colorimetric, etc.), and quantitative onsite

techniques whose preparatory process and/or QC elements are typically less rigorous than those established for definitive data (e.g., X-ray fluorescence, gas chromatography (GC), gas chromatography/mass spectrometry (GC/MS), etc.). Standard analytical methods producing definitive data must also be reviewed for applicability to the project. Input necessary to determine applicable elements for both screening and definitive analytical techniques used include the following at a minimum: defining the contaminants of concern; the concentration range of interest; sensitivity requirements; measurement quality objectives for precision, bias, and completeness; the need and/or type of confirmation necessary; and whether any physical, chemical, or logistical constraints are germane. The appropriate methods may also be dictated by the data user (e.g., outlined by regulatory authority or record of decision.

I.3.2   Measurement quality objectives. To ensure that quality data are continuously produced during analysis and allow the eventual compliance review, systematic QC checks are incorporated into the sampling and analyses to show that procedures and test results remain reproducible and that the analytical method is actually measuring the quantity of target analytes without unacceptable bias. Systematic QC checks include the scheduled analyses of field and laboratory replicates, standards, surrogates, spiked samples, and blanks. Measurement quality objectives (acceptance criteria or ranges) for these systematic QC checks are established to verify DQIs support data usability and contract compliance. The program of systematic QC checks may be viewed from two aspects, batch QC and matrix-specific QC, and are further clarified below.

I.3.2.1   QC checks of known composition samples. General batch QC may be viewed as those QC procedures applied to an interference-free matrix or a matrix of known composition (i.e., blanks, laboratory control samples, single or double-blind performance evaluation (PE) samples, standard reference materials, calibration verification standards, etc.). They ensure the sampling procedures are appropriate and the analytical method are being performed in an in-control mode of operation. These QC checks provide no information on how well the method is performing with respect to the project sample matrix, however. QC checks that exceed measurement quality objective must be clearly documented within the case narrative the along with corrective actions taken*. **It is recommended that contract nonpayment clauses be limited to QC sample results of interference-free or known composition matrices only. An example of a contract nonpayment clause that may be included within project contract documents follows:***

> "The Contractor shall perform chemical analyses in accordance with the requirements established within the specified method and this appendix. When QC checks of an interference-free or known composition do not meet these standards/requirements, corrective action must be taken through proper application of the inspection and services clause. Corrective action may include resampling, repreparation, and/or reanalyses of the affected samples at no additional cost to the Government. If the Contractor fails to promptly perform the required corrective actions, or when the failure cannot be corrected by reperformance, the Government may reduce the contract price or fee payable under the contract to reflect the reduced value of services performed. Continued failure to perform chemical analyses in accordance with these standards/requirements may result in termination of the contract for default."

I.3.2.2   QC checks of matrix-specific samples.

I.3.2.2.1   Matrix-specific (matrix-sensitive) QC procedures should be incorporated into the sampling and analysis protocols to provide information on the precision and bias of the analyses on project samples. These procedures include analyses of field samples in association with surrogate compounds, matrix spikes (MS), matrix spike duplicates (MSD), or matrix duplicates (MD). Matrix-specific procedures performed on other field samples at the laboratory not associated with the project samples are of no value, for they do not provide information on the matrix under observation. It should be noted that MS/MSD/MD analyses may require the submittal of an additional replicate sample to enable the laboratory adequate sample volumes to

perform the requisite analysis. ***For this reason, the project requirements of minimum sample volumes necessary to accommodate the matrix-specific QC samples must be addressed very clearly within the SAP.***

      I.3.2.2.2 Exceedances of measurement quality objective for these types of QC checks may be problematic due to matrix effect (signal enhancement or suppression) on the analysis and should not be viewed as an indicator of poor laboratory performance. For this reason, ***contract nonpayment clauses should not be associated with matrix-specific QC samples.*** However, the laboratory should not use this as an "excuse" to avoid employing proper analytical techniques. The laboratory should make a reasonable effort to overcome matrix interference as noted later in this paragraph. Necessary corrective actions will vary depending on the type of interference, and are subject to analyst professional judgment. ***When these excursions indicate a potential for false negatives, lack of sensitivity, or an inability to accurately detect the target analytes, communication between the laboratory and data user should be pursued to identify alternatives available.*** For instance, procedures to decrease the matrix effect may include implementing cleanup procedures, dilution techniques, smaller sample size processed, etc. However, consequences to the data (i.e., higher detection limits, less representative aliquot, etc.) should also be assessed against project objectives.

      I.3.3 Data quality indicators (DQIs). As previously noted, QC procedures are employed during chemical analysis to support and document the attainment of established measurement quality objectives. Whether these QC procedures support an assessment of general batch control or matrix-specific application, documentation includes calculating DQIs to verify data usability and contract compliance. DQIs were formerly referred to as the PARCCS parameters of precision, accuracy, representativeness, comparability, completeness, and sensitivity. All laboratories conducting analytical work for USACE must be aware of, and be in agreement with, the project DQOs, including the stated DQI - measurement quality objectives. ***To avoid any misunderstandings concerning the level of quality required for the project chemical analyses, the SAP must very clearly delineate all measurement quality objectives for the method QC checks and DQIs (precision, bias, representativeness, comparability, completeness, and sensitivity) for each method applied.*** Tables I-1 through I-8 summarize the measurement quality objectives for eight SW-846 methods. ***These tables may be applied directly to a project, or modified accordingly to define the measurement quality objectives for laboratory DQIs (precision (P) and bias (B)) of the laboratory control samples (LCS), MS, MD/MSD, etc. However, project requirements must still be defined for the remaining applicable DQIs within appropriate project documents (e.g., SOW, SAP), for example, DQI performance objectives of field QC samples (precision objective for field replicates, bias objective for field blanks, bias (accuracy) objective of double-blind PE samples, etc.); DQI performance objectives for matrix-specific sensitivity (per requisite methods); DQI performance objectives for project completeness (note whether field and lab completeness are assessed separately or combined); and qualitative DQIs (representativeness, comparability).***

      I.3.3.1 Precision. Precision refers to the distribution of a set of reported values about the mean, or the closeness of agreement between individual test results obtained under prescribed conditions. Precision reflects the random error and may be affected by systematic error. Precision also characterizes the natural variation of the matrix and how the contamination exists or varies within that matrix. For chemical parameters that do not allow homogenization prior to sample acquisition (e.g., volatile organic analysis), precision values must be reviewed accordingly. ***In order to assess the effect these variables have on the total precision of data, both field and laboratory replicates should be acquired.*** In order to assess matrix heterogeneity or sample handling procedures, field precision is commonly determined from field duplicate samples or quality assurance split samples. For environmental samples, laboratory precision is commonly determined from laboratory duplicate samples (i.e., MS/MSD or MD samples). However, to establish the precision of a given analytical method without the effect of a matrix, a laboratory control sample is necessary. USACE currently recommends the inclusion of a laboratory control sample duplicate within a batch, but does not require it. Statistical measures of precision include relative percent difference (RPD)

(relative range for duplicates), standard deviation, or relative standard deviation. The RPD for a set of duplicate measurements of a variable X is defined as:

$$\text{RPD} = \left\{ \frac{|X_1 - X_2|}{[(X_1 + X_2)/2]} \right\} \times 100\% \tag{I-1}$$

If sufficient replicates are taken from a particular matrix for a project, precision may be expressed as the standard deviation, Percent Relative Standard Deviation (RSD), or Coefficient of Variation (CV). This value assesses the precision of the sample within that population matrix, where n is the number of samples or data:

$$\text{RSD} = \text{CV} = \left(\frac{[\text{std dev}]}{\bar{X}} \right) \times 100\% \tag{I-2}$$

$$[\text{std dev}] = \left[\Sigma (X_i - \bar{X})^2 / (n - 1) \right]^{1/2}$$

I.3.3.2 Bias. Bias refers to the systematic or persistent distortion of a measurement process that causes errors in one direction (above or below the true value or mean). Bias may be affected by errors made in field or laboratory handling procedures. For example, procedural deviations in sample acquisition, incomplete homogenization prior to subsampling, or incomplete extraction of contaminants from the matrix intensifies bias. Bias is a term that is related to but is not interchangeable with accuracy. ***Bias assessments are typically based upon the analysis of spiked reference materials or spiked samples (i.e., LCS, MS, MSD, surrogates).*** When the sample matrix is spiked, the result allows an assessment of the effect of the sample matrix on recoveries. The sources of error contributing to the bias of a measurement can be difficult to determine for an entire sample collection/analysis activity. Sources of error may include the loss (or addition) of contaminants from the sampling and analysis process (i.e., sample handling, field cross-contamination, improper sample preservation, sample manipulation during preparation and analysis), interferences present within the sample matrix, and measurement error (i.e., calibration error or drift). Bias values for the LCS represent quantitative limits beyond which data are unacceptable. Bias values are commonly expressed as percent recovery. Percent recovery (%R) is calculated as follows:

$$\%R = \left[\frac{(X_s - X_u)}{K} \right] \times 100\% \tag{I-3}$$

where

X_s = measured value of the spiked sample

X_u = measured value of the unspiked sample

K = known amount of the spike in the sample

When %R is calculated for LCS or other reference materials, X_u could be set at zero. The relationship between percent bias % B and percent recovery is as follows:

$$\%B = {}^{\star}\%R - 100^{\star} \tag{I-4}$$

I.3.3.3 Accuracy. Accuracy is the measure of the closeness of an observed value to the "true" value (e.g., theoretical or reference value, or population mean). Accuracy includes a combination of random error and systematic error (bias) components that result from sampling and analytical operations.

I.3.3.4 Representativeness. Representativeness refers to the degree to which sample data accurately and precisely describe the characteristics of a population of samples, parameter variations at a sampling point, or environmental condition. Samples that are not properly collected or preserved (e.g., contaminant loss or addition) or are analyzed beyond acceptable holding times should not be considered to provide representative data. ***Representativeness is a parameter that is concerned primarily with the proper design of the sampling program or subsampling of a given sample.*** An assessment of representativeness would include an evaluation of precision. The representativeness criterion is best satisfied in the laboratory by making certain that all subsamples taken from a given sample are representative of the sample as a whole. This would include sample premixing/homogenizing prior to and during aliquotting procedures. Samples requiring volatiles analysis should not undergo any premixing or homogenization. Therefore, noting sample characteristics in a case narrative may assist in the evaluation of data. Representativeness can be assessed by a review of the precision obtained from the field and laboratory duplicate samples. In this way, they provide both precision and representativeness information. Existing project data and geostatistics may be employed to assess the representativeness of a population by defining the continuity of data from point to point. Geostatistical techniques can then be used to predict spatial distribution of contaminants, aid in the development of future project sampling designs, identify sample locations, optimize sample spacing, estimate probabilities, etc. Applicability of representativeness in assessing a contaminant population is improved by using a larger number of samples.

I.3.3.5 Comparability. Comparability is a qualitative objective of the data, expressing the confidence with which one data set can be compared with another. Sample data should be comparable for similar samples and sample conditions. ***This goal is achieved through the use of standard techniques to collect representative samples, consistent application of analytical method protocols, and reporting analytical results with appropriate units.*** Comparability is unknown unless precision and bias are provided. When this information is available, the data sets can be compared with confidence. ***When PBMS methods (i.e., new or modified standard reference methods or field analytical techniques) are employed, comparability becomes a critical and potentially <u>quantitative</u> data quality indicator.*** As noted in Section I.1.3, PBMS methods may employ significant differences from the standard reference method used for that same target analyte or chemical compound class. ***If comparability with standard methods has not been demonstrated, a <u>project-specified</u> percentage of duplicate (split) samples for analysis by the standard reference method should be included.*** This allows an assessment of comparability between data sets by calculating the RPD (or a correlation factor adjustment), thus determining the usability of the performance-based method in supporting project decision making. ***Further recommend establishing (and documenting in the project SAP) a project-specified comparability acceptance criterion (e.g., RPD #30 - 50 percent, assuming a one-to-one correlation) based on the intended use of the data and project objectives.***

I.3.3.6 Completeness. Completeness goals, if defined for individual sampling and analytical protocols, are normally combined to assess the expectations of the project as a whole. Completeness is the percentage of measurements that are judged to be usable (i.e., which meet project-specific requirements) compared to the total number of measurements planned. ***Specified levels of overall (both field and laboratory) completeness, in addition to particular completeness goals for critical samples, should be set as part of the project DQOs in the project SAP.*** It is important that critical samples are identified and appropriate QC maintained to ensure that valid data are obtained in order to secure the requisite type, quantity, and quality of data necessary to complete the project. The desired level of completeness is dependent on the project-specific DQOs. This information will be conveyed to the laboratory within the SOW or project SAP. Planning and communication among all parties involved in the process are crucial in order to achieve high completeness percentages. However, completeness goals of 100 percent are usually unattainable. ***Realistic completeness goals (i.e., 80-95 percent) should be determined based upon the size and complexity of the project.***

I.3.3.7 Sensitivity. The term sensitivity is used broadly here to describe the contract method detection/quantitation/reporting limits established to meet project-specific DQOs. Several limits have been established to describe project sensitivity requirements, such as IDL (instrument detection limits), MDL (method detection limits), PQL (practical quantitation limits), SQL (sample quantitation limit), CRDL (contractor-required detection limits), CRQL (contractor required quantitation limits), etc. The IDL and MDL are considered minimum values for detection for the instrument only, and for the instrument and sample preparation steps, respectively. Both the IDL and MDL are normally based on an interference-free matrix (i.e., reagent water or purified solid), which ignore sample matrix effects on those limits. For this reason, published MDLs or IDLS are presumably not achievable for environmental samples. The PQL is defined as the lowest level that can be reliable measured by routine laboratory operating conditions within specified limits of precision and accuracy. This is considered equivalent to the Method Quantitation Limit as defined in section I.3.3.7.2. The SQL is a term established within the USEPA Risk Assessment Guidance for Superfund (RAGS), and are the limits of interest for reporting data for use in a risk assessment. The SQL is defined as the MDL adjusted for sample-specific action such as dilution or use of varying sample aliquot sizes. The CRDL and CRQL published within Contract Laboratory Program (CLP) methodologies are contractually based levels and do not pertain to instrument sensitivity.

I.3.3.7.1 Method detection limit (MDL). The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. A laboratory shall, at a minimum, perform MDL studies during initial method setups and whenever the basic chemistry of the procedures is changed. The MDLs shall be preparatory method-specific and include any cleanup methods used. Since it is not practical to establish an MDL for each specific matrix received at any given laboratory, MDLs shall be determined for all target analytes in an interference-free matrix, typically reagent water for aqueous samples, and a purified solid matrix (e.g., sand) for soil/sediment samples. The laboratory may determine MDLs using procedures presented in 40 CFR, Part 136, Appendix B, or equivalent statistical approach. The validity of the MDL study is verified per CFR requirements by comparing the analyte values to the calculated MDL. If the analyte values are below the calculated MDL or greater than ten (10) times the calculated MDL, an unacceptable bias may be induced; and the MDL cannot be reported. ***To ensure that valid MDL values are determined, the laboratory shall analyze an MDL check sample by spiking an interference-free matrix with all target analytes at about two times the calculated MDL.*** The MDL check sample shall be taken through all the preparatory and determinative steps used to establish the calculated MDL values, to verify a response is detected. If any of the target analytes are not detected, then the concentration shall be increased in another MDL check sample, and the analysis repeated until the failed target analytes are detectable. The detectable target analyte concentrations shall then be used in lieu of the calculated MDL values to establish the lowest detected concentration for samples taken through all appropriate method procedures. ***The laboratory may then demonstrate continued method detection capability by analyzing the MDL check sample on a quarterly basis, in lieu of the annual MDL study.*** When multiple instruments or confirmation columns are used for the same method, separate MDL studies may be replaced by the analysis of an MDL check sample on all instruments/columns. The MDL check sample shall be analyzed after major instrument maintenance or changes in instrumentation or instrumental conditions to verify the current sensitivity of the method. ***When low-level detection in a project matrix is critical, it is suggested that the laboratory perform a method detection limit study or an MDL check sample in project-specific matrices. This should be done at project start-up in order to accurately assess the detection capability of the method for project samples.***

I.3.3.7.2 Method quantitation limit (MQL). Due to the significant amount of error (approximately ±100 percent) associated with results calculated at the MDL and the fact the MDL may not be attainable within project matrices, the method quantitation limit (MQL) is established at a factor of five to ten times

the MDL for the majority of target analytes, but no lower than three times the MDL for any target analyte. The statistical error (±20-30 percent) associated with this area of the calibration curve is notably reduced from the MDL. The appropriate factor applied to the MDL to establish the MQL is based upon the acceptable amount of error the data user is willing to accept for the data generated. Ideally this MQL should have an associated error comparable to the method-prescribed continuing calibration verification (CCV) acceptance limits. This may not be feasible, however, due to a lower concentration range of interest. This approach, however is not appropriate for multicomponent target analytes. Due to the identification of multicomponent target analytes (e.g., polychlorinated biphenyls (PCBs), chlordane, toxaphene, gasoline, etc.) being based upon a recognizable pattern, the MQL should be based upon the MDL as well as the concentration at which the pattern is reliably "identifiable". Thus the MQL represents the value at which the laboratory has demonstrated the ability to reliably quantitate target analytes within a prescribed performance criterion for the method, and establishes the lowest concentration at which the data may be reported without qualification as an estimated value (i.e., J-flag). *In the absence of project-specific requirements to the contrary, USACE requires the following:*

- *The MQL is set at the lowest standard used for the initial calibration curve (or low-level calibration verification standard) or higher for each target analyte. The lowest standard or low-level calibration verification standard must be at least three times the MDL or greater.*

- *Target analyte values detected and reported below the MQL must be flagged as an estimated quantity (i.e., J-flag).*

I.3.3.7.3 Method reporting limit (MRL). The method reporting limit (MRL) is a threshold value below which the laboratory reports a result as non-detected (U); and must be presented as "less than a concentration value" (< ##) according to the following. When data is used explicitly to support a risk assessment, the MRL must be equivalent to the SQL, which establishes the lowest reporting limit at the MDL adjusted for sample actions (dilutions/concentrations). However, when the data is being used for other purposes that cannot tolerate a high degree of error (including FNs and FPs), the lowest reporting limit must be established following method procedures defined in I.3.3.7.1. This includes data used for remedy implementation, confirmation, no further action (NFA), or site closure. The highest value reported for the MRL is dependant upon project-specified action or decision levels and is discussed in detail in the following section. MRLs are adjusted based on the sample matrix and any sample dilutions/concentrations necessary.

I.3.3.7.4 Project MRLs relation to action levels. When defining appropriate contract requirements for the MRL, the following issues should be considered.

C *The data needs identified by the data user*

C *The uncertainty associated with the low-level data that the user is willing to accept*

C *The sensitivity capability of the method and instrumentation*

The data needs may be associated with compliance issues, establishing action or decision levels for the project. For instance, maximum contaminant levels (MCLs), maximum contaminant level goals (MCLGs), media cleanup standard, or other applicable, or relevant and appropriate requirements. Other data users (e.g., risk assessor) may require a toxicity reference concentration, a preliminary remediation goal, or other concentration of interest. *In general, USACE recommends that the MRLs be established at approximately one-half the expressed project action levels.* This establishes an acceptable degree of confidence in the resulting data to minimize the potential for false positive (type I) and false negative (type II) decision errors in the comparison of data near the stated project action levels.

The range of MRL determinations to support non-risk related data uses is shown in Figure I-1.
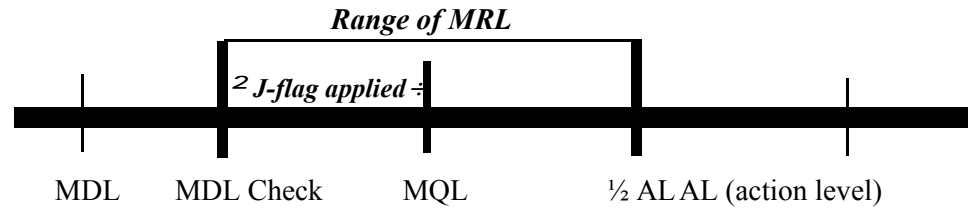

Figure I-1.   Range of MRL determinations to support non-risk related data uses

The range of MRL determinations to support a risk assessment data use is shown in Figure I-2.
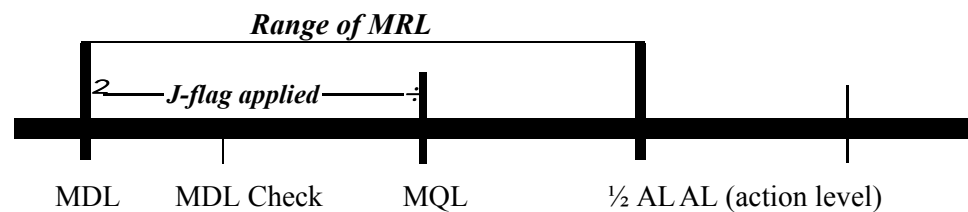

Figure I-2.   Range of MRL determinations to support a risk assessment data use

- C *The project-specific MRLs may be established anywhere in the range from the MDL check sample concentration (two times the MDL) or MDL (adjusted for sample action) up to one-half of the project action level.*

- *When the project-specific MRLs are established below the laboratory MQL for that method, the sample results reported (below the MQL) will be qualified as estimated. If very low levels of quantitation are required (e.g., data used for a risk assessment or compliance issue), to avoid estimation of data based upon this requirement, the following is recommended. Analyze a low-level check sample (taken through the appropriate preparatory procedures) at the MRL level to assess the accuracy at this concentration. An appropriate performance criterion should be defined based upon this assessment.*

- *If the project action levels are near or below the MDLs generated by the laboratory or proposed within the methods, it is unlikely the sensitivity of the method will be achievable for an environmental matrix without imposing method variations. Discussions with USACE or laboratory personnel may be needed to identify options available to lower the MDL of the method (i.e., increase initial sample volumes, decrease final extract volumes, increase sample extract analyzed/injected, etc.), or to select an alternative method.*

- *If the recommended factors cannot be accommodated, the data user is informed of this predicament, and a compromise must be reached. Compromise may entail accepting a higher degree of error associated with the data reported near action levels, or the acceptance of a higher potential for false negatives (type II error) near the MDL.*

I.4   General Laboratory Requirements

Per ER 1110-1-263, each laboratory performing work for USACE shall comply with ISO/IEC Guide 25 (1990). This may be accomplished by the application of the USACE laboratory validation as identified in

ER 1110-1-263. Procedures for the laboratory validation process are described in EM 200-1-1. The following laboratory requirements are pursuant to meeting the standards established within the noted references. ***Individual project requirements may be more or less stringent than those described in the following sections.***

I.4.1   Laboratory quality system. A laboratory must establish, implement, and maintain a quality system appropriate for the type, range, and volume of analytical services it provides. The elements of this quality system shall be documented within a Laboratory Quality Management Plan (LQMP) or related documentation. Laboratory management is responsible for communicating the stated policies and practices to laboratory personnel, ensuring all information is clearly understood and implemented. The laboratory shall perform periodic audits of activities to verify compliance with the quality system. When deviations are discovered, the laboratory shall take immediate corrective action to remedy the situation or practice, notifying any client whose work may have been affected.

I.4.2   Laboratory quality management plan (LQMP). The laboratory shall prepare a written Quality Management Plan, which describes the general and specific procedures used within the laboratory to achieve scientifically valid and legally defensible data. ***This documentation requirement pertains exclusively to the laboratory and is not considered equivalent to the Quality Assurance Project Plan (QAPP), which is an integral part of the project-related SAP.*** However, the laboratory may be required to submit this documentation as an appendix to the project-specific QAPP. ***When conflicting language exists between the project QAPP and the LQMP, the project QAPP takes precedence over the LQMP.*** The Quality Management Plan should present the policies, organization, objectives, functional guidelines, and specific QA and QC activities of the laboratory designed to achieve the data quality requirements when running performance-based methods, such as the SW-846 methods. SOPs pertaining to each element shall be included or referenced as part of this QA Management Plan and should describe the specific operational and analytical procedures as normally implemented by the laboratory. This plan should include, at a minimum, the following elements:

- QA policy, objectives, and commitments, any allowable departures from documented policies.

- Organization structure and personnel — include descriptions of key personnel, identify relationship between management, operations, support, and QA personnel.

- Facilities and equipment.

- Document control — notebook policy, sample tracking and custody procedures, LQMP and SOP organization and control.

- Scope of analytical methodologies provided — sample preparatory and determinative procedures available; methods implementation/calibration procedures and frequency, standards preparation procedures, traceability of measurements and procedures employed, decision processes/procedures/responsibility for initiation of corrective action.

- Data generation — data collection procedures, data reduction procedures, data evaluation procedures, data reporting/authorization procedures.

- Quality control — solvent/reagent checks, reference material analysis, internal QC checks, retesting or corrective action implementation, verification of electronic data management systems.

- QA — determination and monitoring of method QA performance, systems/internal audits, customer complaints resolution, performance/external audits, interlaboratory comparisons and proficiency programs, corrective action procedures, and QA reporting procedures.

Submission of this Laboratory QA Management Plan for review, along with some or all of the SOPs, may be required before sample testing can be initiated on any given project. These documents shall be amended should deficiencies be noted during review or whenever the fundamental elements described previously are updated (i.e., annually).

I.4.3   Laboratory organization, management, and analytical personnel responsibilities. The laboratory shall have sufficient personnel with appropriate education, current training, and experience to fulfill their assigned duties. The laboratory shall promote independence of judgment and integrity with well-defined responsibilities outlined for each individual within the laboratory organization. Personnel training records shall be maintained by the laboratory.

I.4.3.1 Laboratory management. Laboratory management shall at a minimum have a technical director/manager responsible for overall technical operations. The technical director shall have a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline, and a minimum of 2 years of laboratory experience. The laboratory management shall have sufficient authority and resources to fulfill their duties accordingly. Management staff shall be responsible for actively supporting the following at a minimum: implementing the policy and practices defined within the LQMP, maintaining accurate SOPs and enforcing their use in the laboratory, participating in interlaboratory comparisons and proficiency testing, certifying that personnel performing all tests have proper education and training, providing appropriate management and supervisory support to ensure adequate supervision of technical staff, providing a contingency plan that identifies backup personnel for key laboratory positions (i.e., technical director/manager, QA officer/manager, etc.) in the event of personnel absence, having policy and procedures in place that ensure protection of clients' confidential information and proprietary rights, and maintaining a work environment that emphasizes the importance of data quality.

I.4.3.2 Laboratory quality assurance officer. The laboratory shall at a minimum have a QA officer/manager, responsible for the laboratory quality system. The laboratory QA officer shall be responsible for maintaining the quality system and overseeing the QA aspects of the data. The QA officer shall work independently of the laboratory production management and have direct access to the highest level of management for decisions on laboratory policy and resources. In laboratories with limited staff (i.e., <10 technical personnel) the QA officer may also perform duties as the technical director or deputy technical director. QA officer shall at a minimum serve as a focal point for QA issues, perform oversight and QA review for all nonconformance reports, perform QA review for a percentage of laboratory analytical batches or project data packages, evaluate data objectively, independent of laboratory management influence, possess a general knowledge of the methods for which data review is performed, conduct internal audits on the entire technical operation annually, and monitor laboratory method performance by control charts/ranges evaluation, promoting method improvements as necessary. This individual should have a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline and be familiar with all laboratory operations. A minimum of 3 years of laboratory experience, including at least 1 year of applied experience with QA principles and practices in an analytical laboratory, is required. In addition, a working knowledge of general statistical concepts is recommended to support data review and method performance monitoring responsibilities.

I.4.3.3 Organic chemistry section. If applicable, the laboratory shall maintain an Organic Chemistry Section with appropriate personnel, facilities, and instrumentation to conduct the work required. The following disciplines must be clearly represented and staffed as project testing dictates.

I.4.3.3.1   Organic chemistry section supervisor(s). The GC/MS, GC, or Sample Preparation Laboratory Supervisors are responsible for all technical efforts of their respective laboratories, providing sufficient oversight of activities to ensure that data meet all terms and conditions expressed for the project. These individuals shall possess documentation supporting demonstration of performance for all areas for which they provide supervision. In addition, they should have a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline and a minimum of 3 years of laboratory experience, including at least 1 year of supervisory experience.

I.4.3.3.2   GC/MS analyst. Qualifications for these individuals should be a minimum of 1 year of experience in operating and maintaining GC/MS with a bachelor's degree in chemistry or in any related scientific/engineering discipline, or in lieu of the bachelor's degree, 3 years of experience in operating and maintaining the GC/MS and interpreting GC/MS data.

I.4.3.3.3   Gas chromatography (GC)/high performance liquid chromatography (HPLC) analyst(s). Qualifications for these individuals should be a minimum of 1 year of experience in operating and maintaining GC/HPLC equipment with a bachelor's degree in chemistry or a related scientific/engineering discipline, or in lieu of the bachelor's degree, 3 years of experience in operating and maintaining the GC/HPLC and interpreting GC/HPLC data.

I.4.3.3.4   Extraction/concentration technician. Qualifications for these individuals should be a minimum of a high school diploma and 1 year of college general chemistry. These individuals should also have a minimum of 1 year of experience in extraction/concentration.

I.4.3.4 Inorganic chemistry section. If applicable, the laboratory should maintain an Inorganic Chemistry Section with the appropriate personnel, facilities, and instrumentation to conduct the work required for the project. The following disciplines must be clearly represented and staffed as project testing dictates.

I.4.3.4.1   Inorganic section supervisor(s). The metals, wet chemistry, or sample preparation laboratory supervisor(s) is responsible for all technical efforts of the respective laboratories, providing sufficient oversight of activities to ensure that data meet all terms and conditions for each project. These individuals shall possess documentation supporting demonstration of performance for all areas for which they provide supervision.   In addition, they should have a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline and a minimum of 3 years of laboratory experience, including at least 1 year of supervisory experience.

I.4.3.4.2   Inductively coupled plasma (ICP) analyst. Qualifications for these individuals should be a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline with 1 year of experience in operating and maintaining ICP instrumentation, or in lieu of the educational requirement, three additional years of experience in operating and maintaining ICP instrumentation.

I.4.3.4.3   Atomic absorption (AA) analyst. Qualifications of these individuals should be a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline with 1 year of experience in operating and maintaining AA instrumentation for graphite furnace, flame, and cold vapor AA, or in lieu of the educational requirement, three additional years of experience in operating and maintaining AA instrumentation, including graphite furnace, flame, and cold vapor techniques.

I.4.3.4.4   Inorganic sample preparation technician. Qualifications for these individuals should be a minimum of a high school diploma and a college level course in general chemistry or equivalent. These individuals should also have a minimum of 1 year of experience in sample preparation in an analytical laboratory.

I.4.3.5 Wet chemistry analyst. If applicable, qualifications of these individuals should be a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline. These individuals should also have a minimum of 1 year of experience with classical chemistry laboratory procedures in conjunction with the education qualifications, or in lieu of the educational requirement, 2 years of additional equivalent experience.

I.4.3.6 Radiochemical techniques analyst. Qualifications of these individuals should be a minimum of a bachelor's degree in chemistry or any related scientific/engineering discipline with 1 year of experience in performing radiochemical analyses, or in lieu of the educational requirement, three additional years of experience in operating and maintaining radiochemical instrumentation.

I.4.3.7 Technical staff backup. The laboratory should have a minimum of one chemist available at any time as a backup technical person for each analytical area to ensure continuous operations and accomplish the work required. These individuals should have similar education and experience requirements to the primary analyst.

I.4.3.8 Sample custodian and data management. The laboratory should also maintain and staff support positions for Sample Custodian and Data Management personnel. Qualifications for these individuals should be at a minimum of a high school diploma and appropriate on-the-job training.

I.4.4 Laboratory facility and equipment.

I.4.4.1 Laboratory facility requirements. The laboratory shall provide a secure testing facility that can accommodate the proper performance for the type, range, and volume of analytical services it provides. Facility entries must be controlled and monitored as necessary to assure restricted access, especially for areas affecting the quality of activities or data. The design of the facility must provide effective separation of incompatible testing activities and adequate energy sources, lighting, heating/cooling, and ventilation to ensure stability of voltage, temperature, humidity, or other pertinent environmental conditions. This may involve inclusion of an area under positive pressure for analysis of volatile organic compounds (VOC). Adequate monitoring of environmental conditions and general housekeeping should be maintained to avoid any influence on the testing activities performed.

I.4.4.2 Laboratory equipment requirements. The laboratory shall provide sufficient equipment, instruments, and related supplies for proper performance of work. All equipment used shall be reflective of the measurement accuracy necessary. The laboratory shall ensure that all equipment and supplies purchased are inspected, a unique identifier assigned to it, and the equipment verified as compliant with all relevant requirements prior to their initial use. Records of all suppliers used to obtain support services and materials shall be maintained.

I.4.4.2.1 Equipment preventive maintenance. To minimize downtime and interruption of analytical work, preventive maintenance shall be routinely performed on each analytical instrument. Designated laboratory personnel should be trained in routine maintenance procedures for all major instrumentation. When repairs are necessary, the equipment shall be taken out of service, repairs performed by either trained staff or trained service engineers, and an evaluation of the impact on previous calibrations or tests performed. It is generally recommended that maintenance contracts be maintained on all major analytical instruments. Detailed SOPs shall be on file or the information incorporated into method SOPs/LQMP that describe preventive maintenance procedures and schedules. The laboratory shall maintain detailed logs for each instrument documenting the preventive maintenance and repairs performed.

I.4.4.2.2   Equipment backup capabilities. Backup instruments shall be designated in case of an extended breakdown for an analytical instrument. It is the laboratory's responsibility to have a backup plan in force to ensure that all sample holding times can be met. This plan can include rental of backup instruments or the use of another USACE validated laboratory for a given procedure. All equipment outside of the laboratory's permanent control shall be evaluated to ensure that all relevant requirements are met prior to its initial use. ***Before any subcontracting is performed, USACE must be informed and approval given, in writing.*** The laboratory shall ensure, and be able to document, that all subcontractors employed are competent to perform the duties requested and comply with all of the requirements established within this guidance and EM 200-1-1, as appropriate.

I.4.4.2.3   Laboratory equipment records. The laboratory shall maintain appropriate records or documentation for all instruments and support equipment to identify type of equipment; manufacturer's name or equipment make, model, and any serial numbers or unique identifiers; dates received and placed into service; condition when purchased (new, used, etc.); current location; manufacturer instructions/manuals; history of any damage, modification, or repair; instrument maintenance logs; and calibration/calibration verification run logs.

I.4.5   Laboratory SOPs. Laboratories shall be required to maintain written, approved laboratory-specific SOPs for all methods and general operations. Laboratory-specific SOPs that fully detail the actual procedures and documentation used to implement performance-based methods are required. Simply referencing a given method or method number is not sufficient. Overall, these SOPs should be based on the guidance published by USEPA (EPA QA/G-6). The SOPs shall be written narrative, stepwise descriptions of laboratory operating procedures. The SOPs shall accurately describe the equipment and the actual procedures used in the laboratory. Copies of the SOPs shall be readily available to the appropriate laboratory personnel. Calculations that are performed external to an instrument or in its automation software shall be documented in the SOPs. The SOPs should also identify an appropriate estimation of uncertainty for all measurements by the designation of appropriate class/grade of equipment within the SOP, or by the number of significant figures recorded based upon the accuracy of the equipment used. The format for SOPs may vary depending upon the kind of activity for which they are prepared. However, at a minimum, the following sections shall be included: Title/Signature/Effective Date page; Scope and Application; Method Summary; Sample Preservation, Containers, Handling, and Storage; Interferences and Potential Problems; Equipment and Apparatus; Reagents and Solutions; Procedures; Calculations; Quality Assurance/Quality Control; Corrective Actions, Data Evaluation; MDL Studies/Sensitivity Assessment; Health and Safety; Sample Disposal; References; and Example Forms. Laboratory SOPs shall be given unique identification (ID) numbers. These SOPs shall be controlled documents that are reviewed annually or updated as necessary whenever procedure/method changes are made and a new version number assigned. Retired SOPs shall be maintained on file by the laboratory in case data quality questions arise later.

I.4.6   Document control procedures. The laboratory shall maintain records documenting all phases of sample handling from sample receipt to final analysis. Accountable documents used by laboratories include, but are not limited to, logbooks, chain-of-custody records, sample work sheets, bench sheets, instrument printout, and other documents relating to the sample or sample analysis. The laboratory shall use a document numbering and identification system for all documents/logs. All observations and results recorded by the laboratory shall be recorded on either preprinted laboratory forms or permanently bound laboratory logbooks, or entered into secure computer systems. Observations including noting basis for any manual integrations performed are recommended. Pages in both the bound and unbound logbooks shall be sequentially numbered. Preprinted laboratory forms shall contain the name of the laboratory and be dated (month/day/year) and signed by the person(s) performing the activity at the time the activity was performed. Permanently bound laboratory logbooks shall be dated and signed by the person performing the activity at

the time the activity was performed. All logbook entries shall be in chronological order. All entries shall be recorded in indelible ink. Unused portions of the logbooks shall be "z'd" out. Corrections to logbooks shall be made by drawing a single line through the error and entering the correct information. Corrections and additions shall be dated and initialed. Computer forms shall contain the name of the laboratory and be dated and signed by the person performing the activity at the time the form is printed. Computer systems must be established to maintain the integrity of the data, i.e., verified to ensure accurate capture, processing, manipulation, recording, and reporting of data, configured to restrict access and provide for appropriate backups and audit trails, etc. The laboratory shall retain on record all original observations, calculations and derived data, calibration records, and a copy of the test report for a minimum of five (5) years, or as specified by project requirements if longer periods are defined. In the event of laboratory closure, all records shall be transferred to the appropriate USACE clients.

I.4.6.1 Standard preparation log. Standard preparation logs should document the preparation of all calibration standards and spiking standards associated with the respective analysis (e.g., the initial calibration, CCV, and initial calibration verification (ICV) standards as well as the MS, LCS, surrogate, and postdigestion spike (PDS) spiking standards). The laboratory shall maintain complete internal documentation for all standards and reagents used that allows traceability back to the original source. At a minimum, the standard preparation logs must clearly specify the following for all standards:

- Sources (e.g., manufacturer and lot number for commercial stock solutions)

- Composition (e.g., initial and final concentration of all target analytes, type and purity of standards)

- Preparation and expiration dates

- Unique ID number of the standard

- Reagents and solvents added to standards (including source and lot numbers)

- Name of preparer

When a standard is prepared via the dilution of a stock solution, the spiking volume and concentration of the stock solution and the final volume and concentration of the diluted standard should be specified and documented accordingly. Manufacturer certificates for commercially purchased stock standards must be maintained. When the laboratory prepares its own stock solutions, calculations and conversion factors should be shown in the standard preparation log (e.g., a general formula or sample calculations).

I.4.6.2 Sample preparation log. Sample preparation logs should document all significant sample preparation activities. All reagents/standards used shall be clearly identified (e.g., with lot numbers) on the appropriate laboratory bench log sheets. The sample preparation logs must include the following information:

- Sample and batch ID numbers

- Matrix

- Preparatory method (method or laboratory SOP ID number)

- Date of sample preparation

- Initial volume or weight of the sample processed
- Final volume of the sample processed (after digestion, extraction, or cleanup)

C   Percent moisture (for solid samples)

C   Reagents and solvents added to the samples (including source and lot numbers)

C   Any pH and preservation checks and adjustments performed

C   Spiking standards (ID number of the LCS, and MS spiking solutions, volume added, and the final spike concentration)

- Name of analyst

I.4.6.3 Instrument run log. Instrument run logs shall be maintained for each instrument to enable a complete reconstruction of the analytical run sequence. Run sequence logs must indicate the unique identifier appropriated for the instrument used to generate the data, the date of analysis, and the aliquot volume of the sample analyzed (e.g., the injection volume for chromatographic methods). The time of analysis must be specified for chromatographic methods. The order in which field and QC samples are collected and presented should be consistent with the temporal order in which the analyses were performed. Run logs must clearly indicate which field and batch QC samples are associated with each initial calibration, ICV, and CCV. Instrumental analysis logs are particularly important since they provide the basic link between the sample analyses and QC data. Computer logs may be used if all of the preceding information is captured.

I.4.6.4 Computer/instrument outputs. Computer/instrument printouts or other independent information can be incorporated into logbooks if such printouts can be permanently affixed to the appropriate logbook.

I.4.6.5 Electronic data management. Electronic data management systems shall be verified by the laboratory to ensure accurate data transfer, reduction, and reporting. All aspects of the data management system shall be fully documented as compliant with USEPA Good Automated Laboratory Practices (GALP) requirements (EPA 2185).

I.4.7   Laboratory quality assurance procedures. The laboratory shall ensure the quality of results by maintaining an integrated QA system of activities involving the planning, implementation, assessment, reporting, and quality improvement of data. Refer to ISO/IEC (1990) Guide 25 and American National Standards Institute/American Society for Quality Control (1994) for additional information. These activities are typically performed or facilitated by the Laboratory QA Officer and include the performance of periodic audits (system and technical); participation in proficiency testing programs/interlaboratory comparisons, routine analysis of certified reference materials or second source reference materials, and monitoring method performance (sensitivity, precision and bias) through an evaluation of the MDL study or MDL check sample, and batch QC sample (MB, LCS) control ranges/charts.

I.4.7.1 Laboratory audits. As noted in Section I.4.3.2, annual laboratory audits shall be conducted internally for each analytical area to verify the following at a minimum: procedures are compliant with SOPs; documentation practices are complete and traceable to a certified source(s); data reviews are complete, well-documented, and effective; and data reporting practices, including electronic or manual data transfer and client report generation, are accurate and complete. All audit findings, any corrective actions, root cause determination, etc. shall be fully documented in QA reports to management. The QA officer shall document that all corrective actions necessary are verified complete within a reasonable time frame. Audits performed by external agencies or accrediting authorities shall not substitute for internally conducted laboratory audits.

I.4.7.2   Laboratory method performance monitoring using LCS.

I.4.7.2.1   The laboratory shall generate in-house warning (2-sigma) and control (3-sigma) limits for all target analytes from LCSs, defined in Section I.10.2.2. The LCSs are prepared from interference-free aqueous and solid matrices in order to evaluate the quality of the method performance. These "mean" control limits/charts are generated from bias measurements (e.g., LCS recoveries) to assess the method performance and data quality over an extended period of time. The "warning" and "control" limits for mean control charts set at 2-sigma and 3-sigma approximate the 95 and 99 percent confidence intervals, respectively. A minimum of 30 points should be used to establish these control ranges or charts. In addition, data from all analyses (including method failures) should be used to generate the limits to prevent diminishing the ranges by biasing the data input. Outliers may be excluded from the data if proper QA procedures are employed such as using appropriate statistical tests (e.g., Dixon's Extreme Value test, Discordance test). It would not be necessary to maintain graphical control charts for all target analytes. It is recommended that a representative subset of target analytes for each method be chosen for control chart generation to observe method trends. These control ranges should be updated every 6 months, and reviewed by the QA officer annually at a minimum. Additionally, range control charts may be used to evaluate precision between interbatch LCSs. Range control charts set the 95 and 99 percent confidence intervals at 2.456-sigma and 3.268-sigma for the warning and control limits, respectively. *Because so many laboratories mistakenly apply the 2-sigma and 3-sigma factors to calculate precision control limits in lieu of the correct factors noted, caution should be exercised when comparing precision control limits between different laboratories.*

I.4.7.2.2   Evaluate laboratory control limits against the measurement quality objectives presented in the project DQOs, the published reference method, or this guidance to survey the need for method evaluation or modifications. Note the baseline measurement quality objectives summarized in Tables I-1 through I-8 are intended for evaluation of batch control acceptance and may not be reflective of a laboratory overall performance as depicted by their internal control limits. Evaluate the calculated mean for a general assessment of the method systematic bias and review of representative control charts for evidence of analytical trends. Information gathered should be used to troubleshoot analytical problems associated with method implementation, with suggestions offered for quality improvements and corrective action to tighten limits.

I.5   Laboratory Sample Handling Requirements

I.5.1   Sample receipt.   The receiving laboratory's chain-of-custody, sample storage, and dispersement for analysis shall be documented per specific laboratory SOPs and project requirements. *Information on project custody, analysis, and data reporting requirements as noted in the SAP and highlighted on the Laboratory Notification Checklist or similar should be received by the laboratory prior to (or accompanying as with the Laboratory Notification Checklist) the first shipment of incoming samples.* Individual Cooler Receipt Forms or similar shall be used by the laboratory for each cooler to verify sample condition, including proper sample containers, volumes, preservation, etc., and document any problems noted. Corrective action will be required for any deficiencies identified.   Refer to Chapter 3, Figures 3-4 and 3-3, for facsimiles of examples of the laboratory notification sheet, and cooler receipt form, respectively. *It is recommended that all coolers contain at least one temperature blank.* The temperature blank should be a 40-mL volatile organic analysis vial filled with water and placed in a representative position inside the cooler. Multiple vials could be used, if needed. The laboratory should document when the temperature blank was positioned inappropriately or was not representative of the cooler temperature measurement. Sample log-in procedures shall follow the facsimile cooler receipt form (Figure 3-3). The chain-of-custody form, any shipping documents, completed cooler receipt forms, telephone conversation record forms, and any corrective action forms will be maintained by the laboratory for each shipment and included in the reporting package when the results are submitted.

I.5.2   Sample storage. The laboratory shall provide an adequate, contamination-free, and well-ventilated work space for the receipt of samples. All samples and their associated extracts shall be stored under conditions that will ensure their integrity and preservation and are demonstrated to be free from all potential contaminants. Sufficient refrigerator space shall be provided for the proper storage of all samples and their associated extracts. Samples shall not be stored with standards. Samples designated for volatile organics testing shall be segregated from other samples while samples suspected to contain high levels of volatile organics (e.g., underground storage tank soil samples) should be further isolated from other volatile organics samples. ***In the absence of project-specific criteria, samples and their associated extracts shall be stored for a minimum of 60 days after receipt of the final data report for those samples.*** After that time, the laboratory is responsible for the disposal of the samples and their associated extracts in compliance with all Federal, State, and local regulations unless arrangements have been made for the return of any unused sample portions to the site.

I.5.3   Sample security and tracking. The laboratory shall maintain the integrity of the samples received, their associated extracts, and the data generated. Limited and controlled access to all laboratory areas shall be maintained. ***If required by the project, the laboratory should maintain sample and extract chain-of-custody within the laboratory at all times through the use of appropriate documentation and forms; otherwise strict internal chain-of-custody would not be required.***

I.5.4   Sample holding times. Extraction/digestion holding times shall be defined from the date/time of sample collection in the field to the date/time when the sample is first exposed to the extraction/digestion solvent. Analysis holding times shall be defined from the date/time of sample extraction to the date/time of sample analysis. It is required that laboratories maintain documentation that clearly show the dates (and times when applicable) for all sample handling/manipulation processes. Samples should be analyzed as soon as possible after sample collection. Published holding times are generally considered maximum times that samples may be held before analysis and still be considered compliant with method guidelines. Sufficient time should be allowed for the repreparation or reanalysis of samples within holding times should calibration, method, or quality control failures occur.

I.6   General Analysis Requirements

I.6.1   Project application. The requirements presented in this guidance shall be applied to all analytical methods unless specifically overridden by project-specific requirements. Target analyte lists are variable and are dependent upon project-specific considerations. Examples of common target analyte lists are included for eight SW-846 methods.

I.6.2   Method development/initial demonstration of capability. For each method performed, the laboratory shall maintain documentation that demonstrates each analyst's ability to perform the method within the sensitivity and precision/bias limits as stated in the published method, and any requirements outlined within the project SAP. Repeat these procedures when there is significant change in the method, instrumentation, or personnel.   For each new method the laboratory shall perform and maintain documentation for the following:

- Develop a detailed SOP before implementation of that method. Refer to Section I.4.5 for SOP requirements.

- Evaluate method sensitivity by performing an initial MDL study for each matrix per Section I.3.3.7.1. Due to the difficulty in obtaining a solid interference-free matrix for metals determinations, process spiked reagent water for both the aqueous and solid digestion methods

to estimate aqueous and solid MDLs for graphite furnace atomic absorption (GFAA) and ICP analyses.

- Determine an appropriate MQL and MRL for each compound and matrix based upon the calculated MDL and the guidance established in Sections I.3.3.7.2 and I.3.3.7.3.

- Perform an initial demonstration for the method, noting all key employees' (i.e., technicians and analysts) ability to perform the method within the precision/bias limits as stated in the published method. A minimum of four laboratory control samples shall be carried through the method at the same time, or over a period of consecutive days. This control sample shall be obtained from an outside source, if available, or from a lot independent of the calibration standards. The concentration of each target analyte shall be approximately 10 times the MDL. Using the four results, calculate the mean recovery and standard deviation for each parameter or target analyte of interest. Compare the method precision and bias of the laboratory to the method performance summary presented within the published reference method. If any target analytes exceed the acceptance range, the performance is unacceptable. For all unacceptable target analytes or parameters, corrective actions shall be taken to locate the source of the problem, and the test should be repeated. The laboratory must maintain documentation for each analyst performing analysis.

I.6.3   Continuing demonstration of capability. All analysts shall be required to demonstrate their continuing capability to perform any given method by ensuring the following:

- All applicable SOPs are kept current and represent the current implementation of the method by the laboratory.

- The sensitivity of each method is demonstrated quarterly by analyzing the MDL check sample, or annually by an MDL study.

- Any adjustments to the MQL based upon noted changes in method sensitivity are made.

- A minimum of one blind PE sample is analyzed successfully on an annual basis.

- The precision and bias of the method are demonstrated by analyzing laboratory control samples and other QC check samples with each batch of samples processed, and monitored by review of method control ranges/charts.

I.6.4   Data fraud/inappropriate practices. The data produced by a laboratory typically provide the primary basis for environmental cleanup decisions and enforcement actions. The data may also end up in court. *Data must be produced according to the project-specific requirements as specified in the final approved project documents.* The laboratory must be aware of these requirements and be able to show that these requirements were met. Documentation that would clearly show how all analytical values were obtained must be maintained. *The unfortunate aspect of data fraud/inappropriate practices is the inability to readily detect them without significant cost. Project QA procedures employed should be designed to help deter and expose any misrepresentation of data. Refer to Section I.1.2 for information on application of various QA procedures to aid in the prevention of fraudulent activities.*

I.6.4.1   Data fraud. Data fraud can be loosely defined as a gross deviation from contract-specified or method-specified analytical practices, combined with the intent to conceal the deviation. The difference between poor analytical judgment and fraud may be assessed in the documentation of intent within laboratory records. Gross deviations from specified procedures should be investigated for potential fraud, and findings

of fraud should be prosecuted to the fullest extent of the law. The following are examples of fraudulent practices:

- Inappropriate use of manual integrations to meet calibration or method QC criteria. For example, peak shaving or peak enhancement are considered fraudulent activities if performed solely to meet QC requirements.

- Time travel of analyses to meet method 12-hour clock requirements.

- Falsification of results to meet method requirements.

- Reporting of results without analyses to support (e.g., dry-labbing).

I.6.4.2 Inappropriate practices. Several inappropriate practices have also been identified that deserve prudent action. *Issues of this caliber should not be tolerated, and corrective action should be taken immediately to resolve all matters between the laboratory and the data user.* These inappropriate practices may include the following:

- Selective exclusion of data to meet QC criteria (i.e., initial calibration points dropped without technical or statistical justification).

- The repetitive analysis of QC samples and the reporting of only the best result to avoid corrective actions. For example if two or more CCVs are analyzed in an automated run sequence. The last CCV passed but the first CCV fails, then it would be inappropriate to report only the second CCV, and to not perform appropriate corrective actions.

- Multiple instrument or method blanks should not be analyzed prior to other QC samples as a means to address carry-over problems, when these blanks are not analyzed before environmental samples also. QC samples must be analyzed in a manner that is representative of the manner in which environmental samples are analyzed, and not given preferential treatment.

- Misrepresentation of laboratory performance by presenting calibration data or QC limits within data reports that are not linked to the data set reported, or QC control limits presented within LQMP that are not indicative of historical laboratory performance or used for batch control.

- Notation of matrix interference as basis for exceeding acceptance limits (typically without implementing corrective actions) in interference-free matrices (e.g., MB or LCS).

To avoid miscommunication, a laboratory must have an SOP that presents correct procedures for manual integrations. As well as clearly documenting all errors, mistakes, and basis for manual integrations within the case narrative, when manual integrations are necessary. Include corrective actions taken, when necessary, and provide appropriate peer review of this information. *Notification should also be made to the appropriate people so that appropriate corrective actions can be initiated.* It is recommended that laboratories also maintain an electronic audit trail that clearly shows all changes to data, who made the change, date, and why.

I.6.5   Analytical standards preparation and traceability. The laboratory shall have, in-house, the appropriate standards for all target analytes. These standards can either be prepared from neat high purity bulk materials or purchased as certified solutions. A critical element in the generation of quality data is the

purity/quality and the traceability of the standard solutions and reagents used in the analytical operations. Primary reference standards and standard solutions used by the laboratory shall be obtained from reliable commercial sources (i.e., National Institute of Standards and Technology (NIST), USEPA, etc.) to ensure the highest purity possible. Certificates shall be available upon request that verify the purity or concentration of each standard. The use of correction factors for all standards that are not at least 99.9 percent pure for inorganics and 96 percent pure for organics will be required. Care should be exercised in the proper storage and handling of all standards and standard solutions. The laboratory shall continuously monitor the purity or quality of reagents and standard solutions through a series of well-documented procedures. Requirements for standards repreparation shall be based on unacceptable performance. For example, initial calibration standards shall be verified with a freshly prepared ICV. For analyses that allow analytical sequence initiation by a CCV, the frequency of standard repreparation will be based on whether standard performance is compliant with the method acceptance criteria. The quality of CCVs failing to meet method criteria should be verified against a freshly prepared CCV. In general, stock and working standards shall be checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change in concentration. All standards and standard solutions are fully documented to comply with Section I.4.6.2.

I.6.6 Sample screening. It is highly recommended that the laboratory screen samples or extracts by methods of their choice to determine which target analytes are present and at approximately what levels.

I.6.7 Target analyte listings. *Target analyte lists necessary for a project should be identified within project contract documents based upon project-specific DQOs*. However, for instances where a particular SW-846 method is specified but the target analyte list for the method is not, Tables I-9 through I-14 may be used to identify target analyte lists for the following SW-846 methods: 8021, 8081, 8082, 8260, 8270, and 8330. These lists were compiled of target compounds common to the various versions of each SW-846 method, and as noted in SW-846 Chapter 2. Note, however, that the most recent versions of these references may contain additional target compounds not included here. The organic target analyte lists (Tables I-10, I-11, I-12, and I-13) were augmented to include those compounds included within the Target Compound List as defined by the USEPA CLP. *Each list should be reviewed based upon project data needs and edited accordingly. Special considerations for target analyte reporting for the following methods should be evaluated and clearly identified within project contract documentation.*

I.6.7.1 Method 8021: VOC by GC/photoionization detector/Hall electrolytic conductivity detector (HECD). The target analyte list for Method 8021 includes those analytes previously associated with deleted SW-846 Methods 8010 and 8020 and some additional target analytes. *Therefore, depending upon project requirements, the entire 8021 target analyte list or a subset may be specified for the project. The following target analyte lists may apply: the full 8021 target analyte list; HVOs (halogenated volatile compounds) (compound list from deleted Method 8010); AVOs (aromatic volatile compounds) (compound list from deleted Method 8020); or BTEX (benzene, toluene, ethylbenzene, and xylene).*

I.6.7.2 Method 8081: Pesticides by GC/electron capture detector (ECD). *Note whether multicomponent pesticides (i.e., chlordane and toxaphene) are actually analytes of concern.* The additional instrument and method QC samples required for these multiple-component analytes significantly increase the level of effort for this method. *It should also be determined if chlordane quantitation should be performed and reported as technical chlordane or the individual chlordane isomers (i.e., alpha and gamma chlordane).* In the absence of guidance to the contrary, assume that quantitation is required for toxaphene and the individual chlordane isomers (rather than for technical chlordane). Recently promulgated revisions of Method 8081 do not include PCBs as target analytes. Therefore, guidance on PCB reporting is not included here. Reference Section I.6.7.3 for additional information on reporting considerations for PCBs.

I.6.7.3 Method 8082: PCBs by GC/ECD. *Regulatory aspects of PCBs are based upon the quantitation as Aroclors. However, when not used for regulatory purposes and depending upon project requirements, the results may be reported as individual PCB congeners, or the values summed over an appropriate chromatographic range and reported as total PCBs. When weathered PCBs are encountered and the data use requires the use of Aroclors, then the quantitation as Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Peaks within the sample chromatogram not related to PCBs should be subtracted from the total area. Full documentation of this approach must be provided in the case narrative when this option is chosen. Caution should be exercised when using differing quantitation techniques for comparability of project data may be reduced. Studies have shown that concentrations derived from samples quantitated as Aroclors were larger than those determined using the congener method. Due to the potential regulatory aspect and unless otherwise indicated, all samples must be analyzed for the PCB compounds as Aroclors.*

I.6.7.4 Method 8330: Explosives by HPLC. Due to the lack of resolution between 2,4-DNT and 2,6-DNT, and between 2-Am-DNT and 4-Am-DNT, reporting of these compounds may be combined and reported as isomeric pairs.

I.6.8   Analytical methods summary.   The guidance introduces two inorganic (6010, 7010/7470/7471) and six organic (8021, 8081, 8082, 8260, 8270, 8330) SW-846 analytical methods. *The guidance has deliberately omitted method revision numbers from the analytical method designations to enforce its application to any revision of the method in use by USACE. Note also that many of the QA/QC principles and policies included herein apply to methods not directly addressed.* Technical details on the implementation of the eight methods and default limits for performance-based QC parameters are presented. *As noted, these acceptance limits are considered a baseline standard, but they may be modified based upon project-specific DQOs. Reference EM 200-1-2 for information on establishing project DQOs, and EM 200-1-6 for a review of CDQM elements available to aid in the design of a project CDQM program. Project-specific contract documents (e.g., scopes of work, guide specifications, etc.) should reference or identify all applicable analytical methods and QC elements necessary for the project to assure correct and accountable execution of the work.* When this information is not available or adequately defined, then the laboratory shall default to using the latest promulgated revision of the appropriate SW-846 method and application of the QC acceptance limits described herein as the default USACE requirements. The following guidance also outlines general requirements that apply uniformly to all methods by subject heading and any additional parameter or method-specific requirements presented in subsequent sections by chemical parameter, analytical technique, or the individual chromatographic method. For general sample handling procedures used during sample preparation, such as requirements for correct sample homogenizing and laboratory subsampling, refer to the guidance established within Instructions E-4 and E-5, Appendix E.

I.6.8.1 Inorganic analytical methods. The inorganic methods presented focus exclusively on metals analyses. This encompasses inductively coupled argon plasma-emission spectroscopy (ICP), GFAA, and cold vapor-atomic absorption (CVAA) methodologies. Project inorganic method requirements should be clearly identified based on project DQOs. *Note than when the quantitation limit of a metal (e.g., Sb, Pb, As, Tl, and Se by ICP) is higher than the project-required action level, an alternate analytical method capable of achieving a lower quantitation limit for that metal should be used.* Baseline inorganic QC requirements are discussed in subsequent sections by the individual method and summarized in Tables I-1 through I-8. Classical (wet chemistry) techniques are not addressed directly within this guidance. However, the field of conventional, nonmetals analysis involves a variety of instrumental and wet chemical techniques. Instruments include spectrophotometers and other analyzers.

I.6.8.1.1   Inorganic preparatory methods. Several preparatory method options may exist for each determinative method and matrix. However, comparability of the data generated from different preparatory procedures is not guaranteed, nor likely. *Therefore, in order to ensure comparability of data generated throughout the life of a project or between different laboratories, proper preparatory methods must be clearly identified for each chemical parameter/matrix and consistent analytical protocols must be maintained.* Aqueous liquid samples for ICP may be processed by a hotplate technique following Method 3005 or 3010, or by using a microwave technique following Method 3015. Aqueous liquid samples for GFAA are processed by a hotplate technique following Method 3020, or using a microwave technique following Method 3015. *When a comparison of dissolved metals and total recoverable metals results is anticipated, recommend that both the field-filtered and nonfiltered water samples be subjected to the proper digestion procedures (preparatory method) prior to analyses. This ensures a matrix matching of the acid concentrations between the samples. If only dissolved metals results are required, the preparatory method is optional, and analysis by direct aspiration is allowed. Under these circumstances and per method requirements, the calibration standards must be changed to matrix match the samples analyzed. The matching of acid concentrations between samples and standards assures similar viscosity and surface tensions, which affect aspiration characteristics and thus may vary the resulting concentrations.* Solid samples are processed for ICP and GFAA by hotplate following Method 3050, by microwave following Method 3051, or by microwave assisted acid digestion of siliceous and organically-based matrices following Method 3052. Hexavalent chromium digestion should follow Method 3060, and preparatory procedures for the CVAA analysis of mercury are incorporated into the individual analytical methods (7470 for liquids and 7471 for solids). *Proper preparatory procedures to be employed should be identified within the project contract documents (e.g., SOW, SAP, guide specification, etc.). When the method of digestion is not specified, the laboratory must attempt to obtain this information from appropriate USACE project technical personnel.* In lieu of project-specific information, the default preparatory procedures shall follow hotplate techniques following Method 3005 for ICP and Method 3020 for GFAA (3005 for antimony) for aqueous matrices, and Method 3050 for solid matrices. It should be noted that future updates of SW-846 are anticipated to combine these preparatory methods under a common methodology.

I.6.8.1.2   Method 6010. This method is used to determine the concentrations of select metals in the digestates of liquid and solid matrices, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The requirements apply to simultaneous or sequential ICPs. ICPs may be equipped with a torch that is viewed from the radial or axial (e.g., trace ICP) position. For the ICP, mass spectral (MS) detectors are also available.

I.6.8.1.3   Method 7010/7470/7471. The SW-846 7000 series methods are used to determine the concentrations of select metals in the digestates of liquid and solid matrices, employing flame, graphite furnace, gaseous hydride, and cold vapor techniques in conjunction with atomic absorption spectroscopy. This discussion will be limited to GFAA with an appropriate background correction system. Recommend GFAA instruments have a Zeeman background correction capability. *GFAA is commonly used for several elements due to its sensitivity capabilities.* It should be noted that the Update IVA of SW-846 includes all GFAA metals methods combined under Method 7010, all direct aspiration (flame) atomic absorption (FLAA) under method 7000; and has deleted all individual metals methods by FLAA, and GFAA. Mercury shall be analyzed by a cold-vapor AA technique following Method 7470 for waters and 7471 for solids. The AA can be integrated with an appropriate cold vapor accessory for mercury analyses, or independent cold vapor units are also available.

I.6.8.2   Organic analytical methods. The principles and QC requirements established within SW-846 Method 8000 apply to all organic chromatographic methods (e.g., GC, GC/MS, and HPLC methods). Therefore, they are presented generally by topic. *Packed-column methods were formally deleted from SW-*

846 with the promulgation of SW-846 Update III on 13 Jun 1997. These methods, in general, possessed less stringent performance criteria (e.g., column resolution is lower and method QC is less stringent) than their associated capillary column method. *Due to these factors, the laboratory should default to the use of capillary column methods (e.g., Methods 8260B, 8081A/8082, and 8021B for the deleted Methods 8240, 8080, and 8010/8020, respectively).* The laboratory shall not use capillary columns in conjunction with packed column methods in order to apply less stringent QC criterion.

I.6.8.2.1   Organic preparatory methods. Several preparatory method options may exist for each determinative method and matrix. However, comparability of the data generated from different preparatory procedures is not guaranteed nor likely. *Therefore, in order to ensure comparability of data generated throughout the life of a project or between different laboratories, proper preparatory methods must be clearly identified for each chemical parameter/matrix and consistent analytical protocols must be maintained.* Liquid samples may be prepared for extractable organic analyses using a separatory funnel following Method 3510, a continuous liquid-liquid extractor following Method 3520, or solid-phase extraction by Method 3535. Liquid samples for purgeable organic analyses utilizing purge and trap procedures follow Method 5030. Nonaqueous samples should be prepared by solvent dilution techniques following Method 3580 for extractable organic analyses and Method 3585 for purgeable analyses. Solid samples may be processed for extractable organic analyses by soxhlet extraction procedures following Method 3540, automated soxhlet by Method 3541, pressurized fluid extraction by Method 3545, or ultrasonic extraction procedures by Method 3550. For petroleum hydrocarbons and organochlorine pesticides/ PCBs analyses, a supercritical fluid extraction may be used following Method 3560 and 3562, respectively. *Typically, Method 3550 (sonication) is used to prepare solid samples known to have high concentrations of target analytes, whereas Method 3540 (soxhlet), 3541 (soxhtet), or 3545 is generally used in an unknown situation or when low-level concentrations are known or suspected.* Solid samples for purgeable organic analyses utilize Method 5035. *Several notable changes in the protocols covering soil sampling/analysis preparation have occurred with the promulgation of Method 5035. These changes will require a significant increase in the coordination between field and laboratory personnel. Refer to USACE policy guidance (Headquarters, USACE 1998) for details on implementation. When the method of preparation is not specified, the laboratory must attempt to obtain this information from appropriate USACE project technical personnel.* If no information is provided for the project-specific preparatory methods required, the default preparatory procedures for extractable organic analyses shall follow Method 3520 for aqueous samples; Method 3540 or 3541 for solid samples; and those noted previously for purgeable organic analyses. *It is anticipated that project field work will entail the use of proper sample handling protocols that result in the acquisition of a representative sample. These include the use of appropriate sample containers, obtaining sufficient sample volumes, and proper preservation techniques based on the anticipated chemical analyses. Refer to Appendix B for information on proper sample containers, sample volumes, and preservatives necessary. As noted in Section I.5.1 these items are verified upon sample receipt, and any discrepancies notified back through appropriate channels. For chemical parameters that do not allow this assessment during sample login (e.g., VOCs), verification is done post-sample subsampling or analysis, and any problems are noted within the case narrative.* Whenever possible, a quantitative transfer of the entire (1-liter) aqueous liquid sample is made to ensure no loss of target analytes through the adhesion of contaminants on the walls of the sample bottle. A solvent rinse should be performed to avoid this loss. This procedure, however, may not be possible when significant amounts of sediment are present within the water sample. *Due to the problems these fines may invoke on the extraction process, recommend that appropriate project technical personnel be contacted to verify the procedures to employ (e.g., decanting water sample, physical separation of the phases and subsequent analysis of each, etc.).*

I.6.8.2.2   Organic cleanup methods. If significant nontarget interference exists, corrective action shall include implementing appropriate cleanup procedures. Dilution techniques should not be used in preference to cleanup procedures for organic methods. The laboratory shall have a minimum capability of at least one cleanup method for each type of organic analyses for which it provides services. Refer to the individual determinative methods and Method 3600 to identify recommended cleanup methods based on the type and concentration of interferences present, the selectivity of the determinative method, and project method reporting limit requirements. However, analyst professional judgment should also be used to identify appropriate cleanup techniques to employ. *If cleanup procedures are not routinely employed by a laboratory, a formal notification procedure must be in place to advise the client of this.*

I.6.8.2.3   Method 8021. This method is used for the analysis of select VOCs in aqueous and solid matrices by purge and trap device according to methods prescribed previously and subsequently analyzed by GC using an HECD and photoionization detector in series.

I.6.8.2.4   Method 8081.   This method is used to determine the concentrations of select organochlorine pesticides in the extracts of liquid and solid matrices, using fused-silica capillary columns with an ECD. *Method 8081A no longer includes PCBs as target analytes to eliminate the complications inherent in the combined pesticide/PCB analysis. Therefore, PCB analysis must be performed using Method 8082. This may be accomplished by submitting an additional environmental sample for PCB analysis; or the extract may be split prior to implementation of any cleanup procedures, processing individual extract portions for pesticide analysis following Method 8081 and the other portion for PCB analysis following Method 8082.*

I.6.8.2.5   Method 8082. This method is used to determine the concentrations of select PCBs as the seven Aroclors, as individual PCB congeners, or as total PCBs in the extracts of liquid and solid matrices, using fused-silica capillary columns with ECDs. *Refer to project required chemical parameters and Section I.6.8.2.4 in order to determine the necessity for an additional environmental sample for PCB analysis, or the use of an aliquot from the extract (prior to cleanup procedures) for both pesticide and PCB analyses.*

I.6.8.2.6   Method 8260.   This method can be used for the analysis of select volatile organic compounds (most compounds with boiling points below 200 °C) in aqueous and solid matrices by purge and trap device according to methods prescribed previously and subsequently analyzed by GC/MS. Volatile water-soluble compounds can be analyzed with this method but higher quantitation limits may apply. A notable deviation allowed by Method 8260B versus 5030 is the utilization of a heated purge for aqueous samples.

I.6.8.2.7   Method 8270. This method is used to analyze the extracts of aqueous and solid samples for semivolatile organic compounds, also referred to as base/neutral and acid extractables. The extracts are analyzed by GC/MS using a capillary column.

I.6.8.2.8   Method 8330. This method is used for the analysis of select explosives in the extracts of solid and liquid matrices. The extracts are analyzed by HPLC with a UV detector, using C-18 and cyanide reversed-phase columns as the primary and confirmatory columns, respectively. The method specifies extraction procedures for solid samples, and low-level and high-level aqueous samples. In general, aqueous samples for low concentration are extracted by a salting-out extraction procedure using acetonitrile and sodium chloride. Aqueous samples for the high concentration are diluted with acetonitrile, filtered, and analyzed by direct injection. Soil and sediment samples are extracted using acetonitrile in a cooled ultrasonic bath and filtered prior to analysis. *Project-specific approval should be sought for the use of solid*

phase extraction (Method 3535) in lieu of the low-level salting out procedure described in Method 8330,
or the use of a photodiode ray detector as the confirmation technique.

I.7   Preliminary Method Setup

In addition to the general items noted in Section I.6.2, method initiation must include the following
procedures as applicable.

I.7.1   Inorganic analyses - Method 6010.

I.7.1.1 Linear dynamic range. The upper limit of the linear dynamic range for each ICP must be
determined for each analyte wavelength used in order to determine an appropriate concentration for the high
calibration standard. This is done for each analyte by analyzing successively higher standard concentrations
(approximately 3 to 5 standards) until--because of curvature--the highest analyte concentration is
± 10 percent of the "expected" concentration obtained by extrapolating the calibration line from the lower
standards. The concentration chosen for the highest standard must then be chosen below the upper limit of
the linear range. The linear dynamic range must be checked initially and whenever there is a significant
change in instrumental hardware or operating conditions. If the ICP is routinely calibrated using one
standard and a blank, the linear dynamic range must be checked every 6 months.

I.7.1.2 Interelement spectral correction factors. All interelement spectral correction factors must
be determined per method requirements initially and updated at least once every 6 months, based upon failure
of the interelement check standard, or whenever there are significant instrument modifications.

I.7.2   Organic analyses - Method 8000 series. Retention time windows are established to
compensate for minor shifts in absolute retention times as a result of sample loadings and normal
chromatographic variability. The width of the retention time window should be carefully established to
minimize the occurrence of both false positive and false negative results. Tight retention time windows may
result in false negatives or may cause unnecessary reanalysis of samples when surrogates or spiked
compounds are erroneously not identified. Excessively wide retention time windows may result in false
positive results that cannot be confirmed upon further analysis. Retention time windows must be determined
as specified in the latest revision of Method 8000 for all chromatographic methods, except when MS or
Fourier transformed infrared (spectroscopy) detectors are employed. Calculate absolute retention time
windows for each analyte and surrogate for each chromatographic column employed per method instructions.
New retention time windows must be established whenever a new chromatographic column is installed, or
when there are significant changes in the operating conditions. The use of reasonable "default" values,
programmed into instrument software for the width of the retention time window, is allowed if the laboratory
demonstrates that the calculated 3-sigma width is consistently less than the default width, and the default
width is not "excessively large" (i.e., more than 1 to 2 percent of the absolute retention time).

I.7.2.1 Method 8081. Retention time windows must be established as specified in Section I.7.2 for
each surrogate and single-component pesticide target analyte, and for at least three to five characteristic
peaks of multiple-component pesticides. For multicomponent pesticide standards, the analyst should also
rely heavily on pattern recognition and the analyst's experience in the interpretation of the chromatograms.

I.7.2.2 Method 8082. Retention time windows will vary based upon the project requirements for
PCB quantitation as noted in Section I.6.7.3. Absolute retention times will be used when identification of
PCBs as Aroclors is performed. Retention time windows must be established as specified in Section I.7.2
for each surrogate and congeners or for at least 3 to 5 characteristic peaks of each Aroclor. If PCB congeners

are quantitated, normally internal standard calibration techniques are used and relative retention times are determined.

I.8   Instrument Performance Checks

Several methods outline additional QC procedures to verify the instrumentation is in good working condition. These QC samples must be analyzed and meet method-specified acceptable limits prior to commencing sample analyses.

I.8.1   Method 6010 - Interference check standard (ICS). An interference check standard (ICS) must be analyzed at the beginning of the analytical sequence to verify the correction factors established in Section I.7.1.2 are valid. The ICS typically consists of a set of solutions: ICS-A contains only the interferents (at relatively high concentrations) and ICS-AB contains both the interferents and the analytes of interest. The interferents in both solutions must be present at the concentrations that are at least as high as the high-level calibration standard. The ICS-AB solution must contain the analytes of interest (the metals that are not interferents) at concentrations approximately midlevel. The metals of interest in the ICS-AB solution must be within 20 percent of their expected values. When the ICS check is unacceptable, take corrective action to remedy the failure. Check that the background correction factors applied are appropriate, and readjust if necessary. If the ICS fails immediately after the daily initial calibration, recalibrate and reanalyze the ICS. If the ICP can display overcorrections as negative readings, then the ICS-A solution alone may be used to check for interferences. If the analytes of interest are within two times the absolute value of the MDLs (± |MDLs|), the ICS check is acceptable and the ICS-AB solution need not be analyzed.

I.8.2   Method 8081 - Injection port inertness check. Verify injection port inertness by performing percent breakdown checks for 4,4'-DDT and endrin as specified in Method 8081. The midlevel standard containing only endrin and 4,4'-DDT must be analyzed at the beginning of the analytical shift/sequence, before the initial calibration or the continuing calibration verification. If the percent breakdown is not #15 percent for either DDT or endrin, perform injector maintenance (e.g., column clipping). Do not proceed with the calibration or analysis until the percent breakdown for each compound #15 percent.

I.8.3   Methods 8260 and 8270 - Mass spectrometer (MS) tuning. Verify that the MS meets standard mass spectral abundance criteria prior to initiation of any analyses by the injection of BFB (4-bromofluorobenzene) tune standard for Method 8260 and DFTPP (decafluorotriphenylphosphine) for Method 8270. The tune standard must be analyzed at the beginning of the analytical shift/sequence and every 12 hours of continuous analysis. The 12-hour clock starts at the time of injection of the tune standard. Recommend evaluating the ion abundance by using any of the following scan scenarios: use one scan at the apex peak, use the mean of the apex and the preceding and following scans or mean of a symmetric pattern of scans about the apex, or use the average across the entire peak. The tune must satisfy the ion abundance acceptance criteria listed within the appropriate method. Background correction should be compliant with method specifications and employed only for the purpose of correcting for instrument background ions. If a 12-hour tune fails, take corrective action (e.g., clean the MS source) and reinject the tune standard (BFB/DFTPP). Do not proceed with analysis until the tune is acceptable.

I.8.4   Method 8270. In order to verify column condition and injection port inertness, the DFTPP tune standard shall contain appropriate volume of 4,4'-DDT, benzidine, and pentachlorophenol as stated within Method 8270.

I.8.4.1 Injection port inertness check. Similar to Method 8081, the injection port inertness of the GC portion of the GC/MS is evaluated by the percent breakdown of 4,4'-DDT. This procedure is done to

verify acceptable instrument performance, regardless of whether DDT is a target analyte. The percent breakdown of 4,4'-DDT to 4,4'-DDE and 4,4'-DDD should not exceed 20 percent, in order to proceed with calibration procedures.

I.8.4.2   Column performance check. The condition of the GC column is evaluated by the tailing of benzidine and pentachlorophenol. Benzidine and pentachlorophenol must be present at their normal responses, with no visible peak tailing, as demonstrated by the peak tailing factors. The calculation of peak tailing factors can be found on Figure 13 of Method 625, 40 CFR 136, App. A. The acceptance criteria for the peak tailing factor for benzidine is <3.0 and for pentachlorophenol is <5.0.

I.9 Calibration Procedures and Frequencies

The calibration of instruments and support equipment is required to ensure that the analytical system is operating correctly and functioning at the proper precision, bias (accuracy), and sensitivity. ***The frequencies of calibration and calibration verification are presented in the following sections, based upon the various analytical methods and industry standards, or may be changed based upon project-specific DQOs.***

Tables I-1 through I-8 highlight key information on calibration procedures and acceptance limits for each SW-846 method discussed.

I.9.1   Analytical support areas calibration verification. Suggest referring to ASTM D 5522 for additional details on the following procedures and performance criteria.

I.9.1.1   Balances. The calibration of analytical balances shall be verified on first daily use at a mass or masses that bracket or are representative of the measurements routinely performed at that balance. The quality of the weights used for this calibration verification shall be documented and shall be in accordance with the quality requirements established within the referenced ASTM standards. Balance calibration verifications shall be documented in appropriate log books. Acceptance criteria shall be clearly identified. Apply a 1 percent performance criterion to top-loading balances, and 0.1 percent to analytical balances. Refer to ASTM D 5522, ASTM E 319, and ASTM E 898 for additional details.

I.9.1.2   Refrigerators/freezers.   All refrigerators and freezers shall be monitored for proper temperature by measuring and recording internal temperatures on a daily basis. The calibration of all thermometers used for these measurements shall be verified at least annually against NIST-certified or NIST-traceable thermometers. Electronic thermometers shall be calibrated at least quarterly. Temperatures shall be recorded in appropriate log books. Acceptance ranges shall be clearly identified. Maintain refrigerators to 4 °C ± 2 °C, and freezers to -10° to -20 °C. Refer to ASTM Method E 77 for additional details.

I.9.1.3   Pipets and other volumetric labware. All volumetric devices, glassware, or lab ware shall be initially inspected, and all cracked or damaged items removed from use. The calibration of variable-volume Eppendorf-type pipets shall be verified at the volume of use, or at two volumes that bracket the range of use on the day of use, or at a minimum of weekly. The calibration of all fixed-volume Eppendorf-type pipets shall be verified monthly. In addition, the accuracy of all nonstandard lab ware (K-D tubes, Zymark tubes, plastic cups, centrifuge tubes, etc.) used to measure the initial sample volume or final volume of sample extracts/digestates must be verified. Accuracy must be verified to within 3 percent. If the check reveals error greater than 3 percent, steps should be taken to improve the accuracy of these measurements, or use alternative procedures that meet this requirement. It is also recommended that the calibration of all other volumetric glassware (flasks and pipets) be verified at the time of purchase for each lot of lab ware received.

Each calibration check shall consist of at least three measurements, and the average calculated and recorded in appropriate logbooks. Refer to ASTM E 542 and ASTM E 969 for additional details.

I.9.1.4 Water supply system. The laboratory shall maintain an appropriate water supply system that can furnish high-purity water capable of meeting the needs of the various analytical areas. The performance of MBs provides an indication of the source water suitability for the analysis. However, the water supply system should be monitored on a regular basis (i.e., daily or before use) by conductivity readouts or implementation of general chemistry parameters. Appropriate general chemistry parameters should be based upon the analysis performed at the laboratory. Refer to ASTM D 1193 for additional details.

I.9.1.5 Other analytical support equipment. Other support equipment used to maintain appropriate temperatures as prescribed within the analytical method (i.e., hotplates, water baths, etc.) should be monitored for compliance with the method-specified ranges. Recommend notation of any critical times or temperatures on appropriate bench sheets or laboratory logbooks.

I.9.2 Initial calibration curve. An analytical instrument is said to be calibrated when an instrumental response can be related to the concentration of an analyte. This relationship may be depicted graphically, and referred to as a "calibration curve." Initial calibration curves must be established based upon the requisite number of standards identified within the method for each target analyte (and surrogate for organics). As previously described in Section I.3.3.7.2, the method quantitation limit(s) shall be established by the laboratory at the low standard for each target analyte. All reported concentrations for target analytes shall be within the high and low initial calibration standards. Data generated below the low standard shall be reported as estimated (J-flag) values. Data generated above the high standard shall be diluted into the calibration range and reanalyzed. The frequency requirements for the initial calibration vary among the individual methods and are presented in the following sections. Tables I-1 through I-8 highlight key information on initial calibrations by method also.

I.9.2.1 Inorganic analyses. For metals analyses, an initial calibration must be performed at the beginning of each analytical shift, and when a CCV fails or significant instrument maintenance is performed. Linearity is acceptable only if the linear regression coefficient r is greater than or equal to 0.995. If r is less than 0.995, take corrective action and recalibrate. As previously noted, classical (wet chemistry) techniques are not addressed directly. But while calibration and standardization procedures vary depending on the type of system and analytical methodology, the general principles outlined in these calibration sections apply universally. Analytical systems for wet chemistry techniques shall be calibrated prior to analyses being conducted. The calibration consists of defining the working range by use of a series of standard solutions. A minimum of five to seven standards is typically used. The calibration shall be verified on an ongoing basis (every ten to twenty samples at a minimum and at the end of the analysis sequence) to ensure that the system remains within specifications.

I.9.2.1.1 Method 6010. The term standard may refer to a "mixed" standard solution containing all the metals of interest (when the metals are compatible) or to a set of standard solutions where each standard contains a subset of the compatible metals of interest. The initial calibration must be established following one of the following options:

- Calibration option 1. Perform the initial calibration with a high-level standard and a calibration blank. The concentration of the single standard establishes the linear calibration range, and must fall below the upper linear dynamic range of the instrument (see Section I.7.1.1). To ensure accuracy of concentrations at the MQL, verification at a low-level standard is prepared from the primary source standard and results must be within ±20 percent of its expected value. If the

20 percent criterion cannot be consistently met, then the concentration of the daily low-level CCV standard (and associated quantitation limits) should be increased until compliance is attained.

- Calibration option 2. The ICP-AES may be alternatively calibrated with three standards and a calibration blank. Evaluate linearity as described in Section I.9.2.1. The concentration of the low-level calibration standard must be set no lower than the MQL for each analyte. The concentration of the high-level standard establishes the linear calibration range, and must fall below the upper linear dynamic range of the instrument (see Section I.7.1.1).

All standards and samples analyzed shall have a minimum of three exposures with the mean of each set of exposures used for quantitation. The exposure times should be optimized for instrumental response and analysis time. Evaluate the RSD for high-level and midlevel standards and calibration verification standards to < 5 percent. Take corrective action (e.g., recheck the appropriateness of the exposure time) and recalibrate if the QC criteria are not met.

I.9.2.1.2   Method 7010. An initial calibration for GFAA must be established from at least three standards and a calibration blank. CVAA calibration requirements are similar to the standard AA procedures but with a minimum of 5 points. Evaluate linearity as described in Section I.9.2.1. For GFAA a minimum of duplicate injections shall be performed for all standards and samples to improve precision and help reduce furnace pipetting uncertainty. The RPD between duplicate injections for all standards shall be <10 percent. If unacceptable, reanalyze the standard. If still unacceptable, perform instrument maintenance as needed to correct the problem and recalibrate.

I.9.2.2   Organic analyses.

I.9.2.2.1   The initial calibration curve is established as specified in the individual methods, using a minimum of five standards for all single-component target analytes and surrogates, and at least three standards for multiple-component target analytes (e.g., toxaphene, chlordane, and PCBs). Care should be exercised to avoid using inappropriate practices identified in Section I.6.4. Once verified, an initial calibration is valid until a CCV fails or significant instrument maintenance is performed. The shapes of calibration curves are typically a linear function between the concentration of each target analyte to the instrument response. However, many method target analyte listings have been expanded to include analytes that cannot be optimized without application of models for quadratic or higher order mathematical functions. When these models are employed, additional standards must be analyzed to accurately delineate the relationship as outlined in Method 8000B.

I.9.2.2.2   Linearity may be determined using linear regression analysis for each target analyte by calculating the correlation coefficient r. The resulting line would normally not be forced through the origin or use the origin as a calibration point unless it is demonstrated that the intercept of the regression line is not statistically different from zero at the 95 percent level of confidence. Another term used to describe the goodness of fit of the line is coefficient of determination r^2 (the squared correlation coefficient). Alternatively for chromatographic methods, the average calibration factor (CF) or response factors (RF) may be calculated for each target analyte. Linearity may be evaluated by calculating the percent relative standard deviation (%RSD) of the CFs/RFs from the initial calibration standards for each target analyte. Linearity is presumed if the correlation coefficient r is equal to or greater than 0.995, if the coefficient of determination r^2 is equal to or greater than 0.99, or if the %RSD is less than or equal to 15 or 20 percent (depending on the method specifications). A visual inspection of the calibration curve should also be used as a diagnostic tool when nonlinear behavior is observed to verify if there is a large percentage error in any particular portion of the calibration curve. If the visual inspection indicates problems, or if one of these criteria is not met, then

the laboratory shall evaluate the following items for implementation based on an understanding of the detector response/contaminant concentration relationship:

- Check the instrument operating conditions or the initial calibration standards used and make adjustments to achieve a linear calibration curve.

- Narrow the calibration range using the same number of standards as required by the individual method. In general, the highest standard would be lowered first. The consequences of all actions taken must also be addressed, i.e., reduction of the calibration range, raising of the MQL, etc.

- Evaluate the use of a nonlinear calibration curve, when applicable. When nonlinear calibration models are used, the resultant line should not be forced through the origin and the origin should not be used as a calibration point. No higher than a third-order (cubic) calibration model shall be used. Note that when a nonlinear calibration model is employed, more data points are needed to maintain at least three degrees of freedom. For example, use of a quadratic function requires a six-point initial calibration curve. The resulting coefficient of determination r^2 should be greater than or equal to 0.99 for this to be considered acceptable.

- Use of alternative techniques (e.g., relative standard error (RSE)) outlined in the USEPA Memorandum, "Clarification Regarding Use of SW-846 Methods" (EPA/SW-846).

- Despite implementation of these alternatives, method limitations may exist that make the acceptance criteria unattainable for all target analytes. Therefore, SW-846 has incorporated an allowance to evaluate the <u>mean</u> of the RSD values for all target analytes in the calibration if this average value is less than the method acceptance criterion. To avoid the inclusion of target analytes showing gross method failure, this approach may be utilized as long as the target analytes do not exceed the criteria established for poor performers in the method-specific tables (I-1 through I-8). *If the averaging option is employed, the laboratory must communicate the following information within the case narrative to the client: summary of all of the target analytes exceeding method acceptance criteria, the individual RSD results for those compounds, and the mean RSD calculated.*

I.9.2.2.3   Method 8021. Apply the principles as stated in Section I.9.2.2 and summarized in Table I-3. Poor performers for Method 8021 are typically associated with the gaseous compounds and those identified with poor purging efficiency in Table I-9. Marginal failure for %RSD for these compounds shall not exceed 40 percent.

I.9.2.2.4   Method 8081. Several single-component pesticides may coelute on certain GC columns. Therefore, it may be necessary to use two calibration mixtures to ensure sufficient separation for quantitation. Choose calibration mixes to minimize the peak overlap. Surrogates may be calibrated from either mix. For each multiple-component pesticide (e.g., toxaphene), analyze a midlevel standard to aid in pattern recognition. Based upon the positive identification of either compound in the samples, calibrate the instrument for that multicomponent pesticide with a minimum of three standards and reanalyze the extract to enable accurate quantitation. Note that if technical chlordane is required, a separate three-point calibration must be performed using technical chlordane standards. Professional judgment should be employed in conjunction with the method instruction to determine the approach used to calculate the appropriate CF(s) (e.g., the use of total area or selection of a minimum of four to six characteristic peaks for toxaphene and three to five for chlordane). CFs are then used to calculate the mean CFs, standard deviation, and RSD and apply

the principles as stated in Section I.9.2.2 for both single- and multi-component pesticides and as summarized in Table I-4. Marginal failure for %RSD for poor performing compounds shall not exceed 40 percent.

I.9.2.2.5   Method 8082. ***Procedures for initial calibrations will vary based on the project requirements for PCB quantitation as noted in Section I.6.7.3 (e.g., PCBs as Aroclors, PCB congeners, or total PCBs)***. When PCBs are to be determined as Aroclors, external standard calibration techniques should be used; when determined as PCB congeners, an internal standard calibration should be used. Table I-5 summarizes appropriate QC limits.

- Aroclors. The approach taken for an initial calibration will differ depending on the project DQOs. For instance, for projects with a few specific Aroclors associated with the site, recommend the following procedures. Perform the initial calibration using five standards for each Aroclor identified by the project. When samples contain a known mixture of different Aroclors, the analyst may perform a five-point calibration using that Aroclor mixture. When a multipoint calibration is performed for individual Aroclors, calculate and use the calibration factors from a minimum of three to five peaks for those standards and evaluate linearity as presented in Section I.9.2.2. If the PCBs are unknown or the types of PCBs have not been determined, recommend the following procedures. Perform the initial calibration using five standards for a mixture of Aroclor 1016 and Aroclor 1260 standards in order to determine linearity of the detector response. For the remaining five Aroclors, a midlevel standard is analyzed to aid in pattern recognition. Based upon the positive identification of any PCBs in samples corresponding to the Aroclors with only the midlevel standard analyzed, calibrate the instrument for that PCB with a minimum of three standards and reanalyze the extract to enable accurate quantitation. Again, using a minimum of three to five peaks, calculate appropriate CFs for the 1016/1260 and any positively identified PCB standards and apply the principles as outlined in Section I.9.2.2 to evaluate linearity.

- PCB congeners. Table I-11 identifies 19 congeners that have been successfully tested by Method 8082. However, the procedure may be appropriate for additional congeners. When PCB congeners are to be determined, decachlorobiphenyl is recommended for use as the internal standard. Perform a five-point initial calibration using standards containing all PCB congeners. Calculate the RF for each congener in the calibration standards, and evaluate the linearity of the initial calibration using principles as outlined in Section I.9.2.2.

I.9.2.2.6   Method 8260. Apply the principles as stated in Section I.9.2.2, in addition to the following items. Poor performers for Method 8260 are typically associated with the gaseous compounds and those identified with poor purging efficiency in Table I-12. Marginal failure for %RSD for these compounds shall not exceed 30 percent. QC elements and acceptance limits are summarized in Table I-6.

- Verify that the mean RFs for the system performance check compounds (SPCCs) satisfy the minimum RFs requirements specified in Method 8260. If these criteria are not met, evaluate the system (e.g., for standard mix degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system). Take corrective action and recalibrate for all target analytes.

- If the regression coefficient r < 0.965 or RSD > 30 percent for calibration check compounds (CCCs), this is indicative of system leak or column degradation. Take appropriate corrective action (e.g., instrument maintenance) and recalibrate for all target analytes and surrogates.

I.9.2.2.7   Method 8270. Apply the principles as stated in Section I.9.2.2, in addition to the following items. Poor performers for Method 8270 are typically associated with the compounds that exhibit poor chromatographic behavior. Marginal failure for %RSD for these compounds shall not exceed 40 percent. QC elements and acceptance limits are summarized in Table I-7.

- Verify that the mean RFs for the SPCCs satisfy the minimum RFs requirements specified in Method 8270. If these criteria are not met, evaluate the system (e.g., for standard mix degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system). Take corrective action and recalibrate for all target analytes.

- If the regression coefficient r < 0.965 or RSD > 30 percent for CCCs, this is indicative of system leak or column degradation. Take appropriate corrective action (e.g., instrument maintenance) and recalibrate for all target analytes and surrogates.

I.9.2.2.8   Method 8330. Perform the initial calibration as specified in Section I.9.2.2 with the following points considered. Marginal failure for %RSD for these compounds shall not exceed 30 percent. QC elements and acceptance limits for Method 8330 are summarized in Table I-8.

- Due to the lack of resolution between 2,4-DNT and 2,6-DNT, and between 2-Am-DNT and 4-Am-DNT, calibrations of these compounds may be based on "isomeric pairs." Improved resolution may be obtained using a Supelco C-18 column with an eluent of 55/45 (v/v) methanol/water at 0.8 mL/min.

- The C-18 column may be substituted with a C-8 column (as the primary column) if 2-NT and 4-NT are not target analytes or project-specific approval is obtained.   (These two analytes generally coelute on C-8 columns.) Note that a C-8 column must not be used in place of the confirmatory CN-column.

I.9.3   Initial calibration verification. The initial calibration curve shall be verified as accurate with a standard purchased or prepared from an independent source. This ICV involves the analysis of a standard containing all of the target analytes, typically in the middle of the calibration range, each time the initial calibration is performed. The percent recovery of each target analyte in the ICV is determined from the initial calibration and compared with the specifications for the CCV in each method (except for mercury by CVAA) as outlined in Tables I-1 through I-8.

I.9.3.1   Method 8081. A separate ICV standard is required for each multiple-component target analyte (e.g., toxaphene and chlordane) if a calibration is performed based upon its presence in samples.

I.9.3.2   Method 8082. The ICV standards may be limited to contain a mixture of Aroclors 1016 and 1260 or the project-specified Aroclors.

I.9.4   Initial calibration blanks (ICBs) and continuing calibration blanks (CCBs). ICBs and CCBs are required for inorganic metals analyses to verify the system is free of contamination. The frequency of ICB/CCB analyses is presented in Tables I-1 and I-2 as prescribed within SW-846 Methods 6010 and 7010/7470/7471. The concentrations of each target analyte in the ICB/CCB must be less than or equal to the MDL as presented in Tables I-1 and I-2. Samples must not be analyzed until the ICB is acceptable, and all results must be bracketed by passing CCBs to be considered valid.

I.9.5   Continuing calibration verification (CCV). CCVs are analyzed to determine whether the analytical system is working properly, and if a new initial calibration (and the reanalysis of sample extracts) is required. Calibration verification differs in concept and practice from continuing calibration. In this latter technique, a standard is analyzed and new response factors are calculated, or a new calibration curve is drawn from the analysis of the continuing calibration standard. The former verifies compliance with the initial calibration curve, but does not overwrite the response factors used for the quantitation, nor allows resloping of the calibration curve. Calibration verification shall be used for all analytical methods, calculating a percent drift when the initial calibration is based on regression analysis, and a percent difference when the initial calibration is determined based upon %RSD values. CCV typically involves the analysis of a single primary source standard in the middle of the calibration range, between the concentrations of low-level and midlevel calibration standards. The frequencies of the CCV vary between methods but are related to the type of detector used and sample matrices analyzed. The analysis of more frequent CCVs is recommended for very sensitive detectors and when analyzing difficult matrices. This frequency is typically presented within SW-846 methods as at the beginning of the analytical shift/sequence; every 12 hours of analyses or every 10 to 20 samples; and may include at the end of the analytical sequence. Refer to Tables I-1 through I-8 for details on requirements for CCV implementation and acceptance limits for the individual methods. If these QC criteria are not met, take corrective action to inspect the analytical system to determine the cause and perform instrument maintenance to correct the problem before analyzing a second CCV. If the second CCV is acceptable after system maintenance is performed, recalibration is not required but all sample extracts analyzed after the last acceptable CCV must be reanalyzed. If however, the second CCV fails, a new initial calibration must be performed and all associated sample extracts reanalyzed.

I.9.5.1   Inorganic analyses. A calibration verification pair of a CCB and CCV must be analyzed after every 10 samples (including batch QC samples) and at the end of the analytical sequence as outlined in Sections I.9.4 and I.9.5. Refer to Tables I-1 and I-2 or a summary of CCV implementation and QC requirements.

I.9.5.2   Organic analyses. Calibration verification must be analyzed as outlined in Section I.9.5 and as summarized in Tables I-3 through I-8, in addition to the following:

- For certain organic analyses, additional CCVs at low- and high-level concentrations are recommended, due to the instability of their detectors (e.g., HECD, ECD). Measurement quality objectives (acceptance limits) for the high-level CCV should be in accordance with the midlevel CCV criteria. ***This criterion, however, may not be achievable for the low-level CCV. Therefore, no measurement quality objectives for low-level CCVs are included at this time, and should be identified within project documents based upon the use of the data. For instance, if low-level detection is critical based on project action levels or decision levels, appropriate measurement quality objectives should be determined based on an acceptable level of error to support the use of the data.***

- For methods that contain multicomponent target analytes (e.g., PCBs), typically only a subset of these analytes would be used in the CCV.

- For GC/HPLC methods, concepts similar to that presented for initial calibrations apply. However, methods may possess limitations for certain target analytes that make the stated method acceptance criteria unattainable.   Therefore, SW-846 has incorporated an allowance to evaluate the <u>mean</u> of the percent difference (%D) or percent drift values for all reported target analytes in the calibration verification standard to verify whether it is less than the method acceptance criteria. To avoid the inclusion of target analytes showing gross method failure, this approach may be utilized as long as

the target analytes do not exceed the criteria established for poor performers in the method-specific tables (I-3 through I-8). *In addition, the laboratory must communicate this information within the case narrative to the client. Provide a summary of all of the target analytes exceeding method acceptance criteria, the individual %D values for those compounds, and the mean %D calculated.*

• For GC/HPLC methods, compare the retention time of each analyte in the CCV with the absolute retention time windows established in Section I.7.2. Each analyte must fall within its respective retention time window. If this criterion is not met, the chromatographic system must be adjusted to allow another CCV to meet the criterion, or a new initial calibration performed and new retention time windows established.

I.9.5.2.1   Method 8021. Due to the instability and potential drift of the electrolytic conductivity detector (HECD), the following procedures are highly recommended. When analysis includes the HVO target analytes, suggest alternating the midlevel CCV with high- and low-level CCVs as noted in Section I.9.5.2.

I.9.5.2.2   Method 8081. Due to the instability and potential drift of the ECD, the following procedures are highly recommended. Suggest alternating the midlevel CCV with high- and low-level CCVs as noted in Section I.9.5.2, and also recommend incorporating periodic multi-component pesticide CCVs (i.e., toxaphene and chlordane), when applicable.

I.9.5.2.3   Method 8082. When quantitating for PCBs as Aroclors, a midlevel CCV standard containing a mixture of Aroclors 1016 and 1260 (or Aroclors of interest) must be analyzed. When quantitating for individual PCB congeners, the CCV standard must contain all congener target analytes. Due to the instability and potential drift of the ECD, the following procedures are also highly recommended. Suggest alternating the midlevel CCV with high- and low-level CCVs as noted in Section I.9.5.2.

I.9.5.2.4   Methods 8260 and 8270. Apply the principles as stated in Section I.9.5.2, in addition to the following items. It is further recommended that a CCV be analyzed at the end of the analytical sequence.

• Evaluate the RFs of the SPCCs in the CCV. If the SPCCs do not satisfy the minimum response factor requirements specified by Method 8260/8270, take corrective action and reinject the CCV. However, if CCV remains unacceptable, a new initial calibration must be performed.

• Evaluate the responses and retention times of the internal standards in the CCV as soon as possible. If the retention time for any internal standard changes by more than 30 seconds, or the extracted ion current profile area changes by a factor of two (-50 percent to +100 percent) from that of the midpoint standard of a current initial calibration, inspect the mass spectrometer for malfunctions and take corrective action. Reanalyze any affected samples if required.

• Evaluate the concentration of each target analyte and surrogate in the CCV. Verify that the percent drift or percent difference for the CCCs and all project-specified contaminants of concern are within ± 20 percent of their expected values. Evaluate remaining target analytes to assess instrument stability and survey the need for performing instrument maintenance.

I.10 Laboratory Quality Control Procedures

Laboratory overall method performance shall be monitored by the inclusion of various internal quality control checks that allow an evaluation of method control (batch QC), and the effect of the sample matrix on the data being generated (matrix-specific QC). Batch QC is based on the analysis of a laboratory control sample to generate accuracy (precision and bias) data and MB data to assess the potential for cross-contamination. Matrix-specific QC shall be based on the use of an actual environmental sample for precision and bias determinations from the analysis of MSs, MS duplicates, matrix duplicates, and surrogate spikes, etc. Site-specific PE samples could also be used, if available. The overall quality objectives are to implement procedures for laboratory analysis and reporting of data that are indicative of the degree of quality consistent with their intended use. ***Measurement quality objectives given as QC sample acceptance limits and ranges may be default values established within this guidance, or may be based upon project DQOs.*** Laboratory-generated control ranges are also used for an internal evaluation of method performance and control. ***Deviations from any of these target ranges will result in the implementation of appropriate corrective measures and an assessment of the impact on the usability of the data in the decision-making process.***

I.10.1   Sample batching. The basic unit for application of laboratory quality control is the batch. Samples shall be prepared, analyzed, and reported in batches and be traceable to their respective batches. Batch sizes are normally limited to 20 field samples of a similar matrix but can exceed this by incorporating additional QC samples. Each batch shall be uniquely identified within the laboratory. Samples prepared together would normally be analyzed together on a single instrument. Samples taken from the same site would normally be grouped together for batching purposes within the constraints imposed by the method holding times. However, laboratories may find it necessary to group multiple clients' samples into a single batch. Under these circumstances, additional batch QC samples may be needed that evaluate the effect of the matrix from each site on method performance. Field QC samples, i.e., trip blanks, rinsates, etc., shall not knowingly be used for batch QC purposes.

I.10.1.1   Preparation batch. The preparation batch shall be defined as samples of the same or similar matrix that are prepared together by the same person or group of people within the same time period or within limited continuous time periods, following the same method, using the same type of equipment and same lots of reagents. The laboratory shall have sufficient quantities of extraction/digestion lab ware to meet these requirements. Each preparation batch shall contain the requisite number and type of calibration solutions, blanks, QC samples, and regular analytical samples as defined by the analytical method. These requirements shall be completely defined in the laboratory SOPs and are summarized in part in the following sections. The use of cleanup methods would be included as part of the preparation batch. All field and batch-specific QC samples within the batch should be subjected to all preparatory and cleanup procedures employed.

I.10.1.2   Analysis batch (sequence).

I.10.1.2.1   The analysis batch or sequence or instrument run sequence shall be defined as samples that are analyzed together within the same time period or in continuous time periods on one instrument under the control of one continuing calibration verification. Analysis sequences are bracketed by the appropriate continuing calibration verification standards and other QC samples as defined by the analytical method. In general, if an instrument is not used for periods of time or shut down (e.g., overnight, etc.), then a new analysis sequence shall be initiated. Each analysis sequence shall contain the requisite number and type of calibration solutions, QC samples, and regular analytical samples as defined by the analytical method. These

requirements shall be completely defined in the laboratories' SOPs and are summarized in part in the following sections.

I.10.1.2.2 For samples that are purged and then analyzed immediately, the preparation batch and analysis sequences are combined. For this situation, the batch would normally be defined by the loading of samples into the various purge tubes. This definition has been interpreted differently however. For instance, the loading of purge tubes may be performed all at one time, or may continue throughout the day.   In order to ensure ambient environmental conditions throughout the potential loading process, USACE requires a minimum of an MB run every 4 hours, or twice a day when samples are loaded throughout the day.

I.10.2   Preparation batch QC samples. A summary of the minimum required QC samples for each preparation batch follows. All calibrations and QC samples analyzed shall be uniquely identified and traceable to that unique sample preparation batch. Additional QC samples may be required for other batch types based upon project DQOs.

I.10.2.1   Method blank (MB). MBs are analyzed to assess background interference or contamination that exists in the analytical system that might lead to the reporting of elevated concentration levels or false positive data. The MB is defined as an interference-free blank matrix similar to the sample matrix to which all reagents are added in the same volumes or proportions as used in sample preparation and carried through the complete sample preparation, cleanup, and determinative procedures. For aqueous analyses, analyte-free reagent water would typically be used. For soil analyses, a purified solid matrix (e.g., sand) would typically be used, except for metals analyses. The results of the MB analysis are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for that batch of samples. Refer to Section I.11.4.1 for measurement quality objectives/corrective action scenarios for the MB. Sample results shall not be corrected for blank contamination.

I.10.2.2   Laboratory control sample (LCS). The LCS is analyzed to assess general method performance based on the ability of the laboratory to successfully recover the target analytes from a control matrix. The LCS is similar in composition to the MB. Aqueous analyses use analyte-free reagent water. For soil analyses, a purified solid matrix (e.g., Ottawa sand, sodium sulfate, or other purified solid) would typically be used. However, due to the difficulty in obtaining a solid matrix that is metals-free, analyte-free reagent water is taken through the appropriate digestion procedures for metals analyses. The LCS is spiked with all single-component target analytes before it is carried through the preparation, cleanup, and determinative procedures. *A subset of the single-component target analytes containing the specific analytes of interest can be substituted for the full list of target analytes if specified in project-specific contracts or work plans. When multicomponent target analytes are reported, a separate LCS may be necessary if specified by project documents. For Method 8082, the LCS must be spiked with at least one PCB (e.g., 1016/1260 mixture), any project-specified PCBs, or all congeners to support the LCS evaluation.* The use of solid standard reference materials as the LCS is discouraged for they do not typically include all target analytes, and the acceptance limits associated with them are wide due to the heterogeneity of the spiked matrix. Suggest instead the use of an interference-free matrix (e.g., purified solid or sodium sulfate). When samples are not subjected to a separate preparatory procedure (i.e., purge and trap VOC analyses, or aqueous Hg analysis), the CCV may be used as the LCS, provided the CCV acceptance limits are used for evaluation. *The spiking levels for the LCS would normally be set at the project-specific action limits assuming that the low standard used for the initial calibration was below this limit. If the low standard used was at this limit or if the site action levels were unknown, then the spiking levels would be set between the low- and mid-level standards.* The results of the LCS are evaluated, in conjunction with other QC information, to determine the acceptability of the data generated for that batch of samples. Refer to Section I.11.4.2 for measurement quality objectives/corrective action scenarios for the LCS. The

laboratory shall also maintain control charts or tables for these samples to monitor the precision and bias for the method as outlined in Section I.4.7.2. The precision may be evaluated by comparing the results of the LCS from batch to batch, or by duplicate LCSs. Duplicate LCSs within the same batch are not required, but recommended by the USACE.

I.10.2.3   Matrix spikes (MS). The MS is used to assess the performance of the method as applied to a particular project matrix. A MS is an environmental sample to which known concentrations of certain target analytes have been added before sample manipulation from the preparation, cleanup, and determinative procedures have been implemented. ***Reference project-specific documents for the contaminants of concern, guidance presented in the following sections, or the preparatory and determinative methods to determine target analytes to include within the MS spiking solution.*** If no information is available, include all target analytes within the MS. The spike concentrations of the target analytes would normally be set at the same level as the LCS. ***If target analytes are known to be present in samples from a given site, then the spiking level should be adjusted to a concentration that is approximately two to four times the concentrations of the original target analytes.*** For solid samples, care should be taken to ensure that the original field sample is properly divided into homogeneous fractions when allowed by the method. ***Aqueous samples require the submittal of an additional sample for several chemical parameters, especially organic analyses. Therefore, the sample to be used for the MS should be based on project-specific DQOs and specified in the field to ensure that sufficient sample is available to perform the test.*** From the laboratory perspective, preparation batches require MS frequency at one per preparation batch. The merging of these MS frequencies is often difficult for the laboratory to implement. For instance, batches consisting of samples from multiple sites may require additional MSs to meet project requirements of evaluating the samples within the batch because an MS from one site cannot be used to evaluate the matrix effects on samples from other sites. ***Projects must consider the method(s) employed, previous knowledge of the matrix, and other matrix-specific QC samples to help decide an appropriate frequency for MSs for a given project. As a consequence, an MS may not be included with each shipment of samples submitted to the laboratory. Communication between project and laboratory personnel is essential.*** The results of the MS are evaluated in conjunction with other QC information to determine the effect of the matrix on the bias of the analysis. Refer to Section I.11.4.3 for measurement quality objectives/corrective action scenarios for the MS. ***When critical decisions are based on the MS sample recoveries, control charts could be maintained for these samples to monitor the bias of the method for each particular matrix***. Sample results shall not be corrected for MS QC excursions.

I.10.2.3.1 Method 6010. ***Unless superseded by project DQOs, it is not necessary to perform matrix spikes for Na, K, Ca, and Mg for aqueous samples or Na, K, Ca, Mg, Fe, Mn, and Al for soil samples.*** The native concentrations of these low-toxicity metals are usually relatively high.

I.10.2.3.2 Method 8081.   The MS should be prepared for all single-component pesticides. ***Multicomponent pesticides need not be included within the MS, unless required by project DQOs.***

I.10.2.4   Matrix duplicates (MD) or matrix spike duplicates (MSD). The MD or MSD is used to assess the performance of the method as applied to a particular matrix and to provide information on the homogeneity of the matrix. An MSD is a duplicate of the MS as previously described. An MD is an environmental sample that is either divided into two separate aliquots by the laboratory, or requires the submittal of an additional sample. When applicable, care should be taken to ensure that the sample is properly divided into homogeneous fractions. Both the MD and MSD are carried through the complete sample preparation, cleanup, and determinative procedures. ***The requirements for the frequency of MDs or MSDs would normally be specified in the project-specific DQOs.*** The normal use of these QC samples would follow the same requirements as described for the MS. ***In the absence of project-specific DQOs, an***

MD would normally be included with each preparation batch of samples processed where target analytes were expected to be present (e.g., inorganic methods). An MSD would normally be included with each preparation batch of samples processed where target analytes were not expected to be present (e.g., organic methods). The results of the MD or MSD are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the precision of the analysis. Refer to Section I.11.4.4 for measurement quality objectives/corrective action scenarios for the MD or MSD. Control charts can be maintained for these samples to monitor the precision of the method for each particular matrix if required by the project.

I.10.2.5   Surrogates.

I.10.2.5.1 Surrogates are analyzed to assess the ability of the method to successfully recover these specific nontarget analytes from an actual matrix. Surrogates are organic compounds that are similar to the analytes of interest in chemical behavior but are not normally found in environmental samples. Surrogates to be used are identified within the determinative methods. Other compounds may be chosen and used as surrogates, depending on the analysis requirements, whether they are representative of the compounds being analyzed, and whether they cover the chromatographic range of interest. These compounds should be spiked into all samples and accompanying QC samples requiring GC, liquid chromatography, or GC/MS analysis prior to any sample manipulation. As a result, the surrogates are used in much the same way that MSs are used, but cannot replace the function of the MS. The results of the surrogates are evaluated, in conjunction with other QC information, to determine the effect of the matrix on the bias of the individual sample determinations. Refer to Section I.11.4.5 for measurement quality objectives/corrective action scenarios for surrogates. Control charts or tables shall be maintained for surrogates contained within the LCS or MB to monitor the accuracy of the method for each particular matrix. Sample results shall not be corrected for surrogate excursions.

I.10.2.5.2 Explosives analysis by Method 8330 is an exception, in that the surrogate used is actually a target analyte. Care should be exercised by the laboratory with the choice of surrogate used, for the potential remains for coelution with target analytes present within the samples. If 3,4-DNT is used as the surrogate, it must not coelute with TNT. If it is not possible to obtain adequate resolution between 3,4-DNT and TNT, another surrogate should be chosen (e.g., 1,2-DNB).

I.10.2.6   Standard reference materials. The laboratory is encouraged to analyze additional natural matrix standard reference materials and participate in external PE programs.

I.10.3   Analysis sequence QC samples. Certain inorganic analyses (metals by ICP and GFAA) incorporate the following additional QC samples to assess method performance without the influence of the preparatory procedures.

I.10.3.1   Post digestion spikes (PDS). PDSs are performed on every sample as a recovery test for Method 7010, and one per batch (one the sample chosen for MS) for Method 6010. However, duplicate injections of each environmental sample may be avoided when the PDS is performed for each sample for ICP analysis following Method 6010. PDSs are prepared by the addition of the primary source standard to an aliquot of the digestate for the same metals and at approximately the same concentration as is used for the MS - i.e., between the low and mid-level standards. Refer to section I.11.4.6 for measurement quality objectives/corrective action scenarios for PDSs.

I.10.3.2   Serial dilutions (SD). A 5X (1:4) SD test may be performed for an analyte to evaluate matrix interference if the analyte concentration in the original (undiluted) sample is at least 50 times the

MDL. SD-matrix effects are suspected if the RPD between the undiluted and diluted result is greater than 10 percent. If this criterion is not met, further confirmation of the interference via implementation of PDS is necessary when matrix interference is suspected, and the calculation of the result through the use of method of standard additions when matrix interference is suspected/confirmed.

I.10.3.3   When SDs are used to address matrix interference, only "best" diluted results (i.e., the lowest dilution that yielded acceptable results) need be reported. However, the reported result must be qualified (i.e., D-flag) and the dilution factor specified. The associated MQLs or MRLs must also be adjusted based on the dilution factor.

I.11 Measurement quality objectives and Corrective Actions

When errors, deficiencies, or out-of-control situations exist, the laboratory's QA program shall include a system of QC activities that measure the system performance to verify that it meets stated requirements and objectives. When the analytical system performance does not meet defined standards, the laboratory shall employ systematic procedures, called corrective actions, to resolve problems and restore proper functioning to the analytical system(s). Laboratory personnel are alerted that corrective actions are necessary under the following conditions:

- QC data are outside the measurement quality objectives for precision and bias.

- Blanks or laboratory control samples contain contaminants above acceptable levels.

- Undesirable trends are detected in spike recoveries or RPD between duplicates.

- There are unusual changes in method detection limits.

- Deficiencies are detected by the QA department during internal or external audits or from the results of PE samples.

- Inquiries concerning data quality are received from a project manager.

Corrective actions are often handled at the bench level by the analyst, who reviews the sample preparation procedures for possible errors and checks the instrument calibration, spike, calibration mixes, instrument sensitivity, and so on. If the problem persists or cannot be identified, the matter is referred to the laboratory supervisor, manager, or QA department for further investigation. *Poor performance by the laboratory may result in payment penalties or work being repeated at the contractor's expense. Once resolved, full documentation of the corrective action procedure shall be filed with the project-specific records.* The following identifies measurement quality objectives and the corrective actions necessary. When qualification of data is necessary (e.g., flagging), refer to Section I.13.3 for details on flagging conventions. The following shall be required in the absence of project-specific requirements:

I.11.1   Incoming samples. Problems noted during sample receipt shall be documented on an appropriate form (the "Cooler Receipt Form"). *The project manager or appropriate technical personnel shall be contacted immediately for problem resolution.*

I.11.2   Sample holding times. *If samples cannot be prepared or analyzed within the method-required holding times, the project manager or appropriate technical personnel shall be immediately notified so that an appropriate corrective action plan can be generated. If holding times are exceeded and*

results reported, the resulting data shall be flagged, and a discussion of the impact included within the case narrative.

I.11.3   Instrument calibration. Sample analysis shall not be allowed until all initial calibrations, initial calibration verifications, and instrument blanks meet the appropriate requirements. All CCVs that do not meet method requirements shall result in a review of the calibration, rerun of the appropriate calibration standard for the failed analytes, and, if necessary, reanalysis of all samples affected back to the previous acceptable CCV check for the target analytes that failed. Continued failure of the CCV shall result in the construction of a new initial calibration curve followed by the reanalysis of all samples affected. *If results are reported when a calibration criterion has been exceeded, then all results reported shall be flagged, and a discussion of the impact included within the case narrative.* Instrument blanks should be implemented as outlined in the prescribed method.

I.11.4   Method QC samples. Each preparatory batch and analysis sequence must include the appropriate batch and matrix-specific QC samples and standards: i.e., MBs, LCSs, MSs, MDs, MSDs, surrogate spikes, and other method-specified QC. *All QC shall meet the appropriate project-specific measurement quality objectives and associated corrective actions.* In the absence of such criteria or actions, the corrective actions as described in the following sections shall be required. Failure of method QC shall result in the review of all affected data. If no errors can be noted, the affected sample(s) may need to be reanalyzed or reprepared and reanalyzed within method holding times, if possible. *All repreparation and reanalysis necessary due to method failure shall be performed at no cost to the Government. If the situation is not corrected and results reported, then the corresponding data shall be flagged and a discussion of the impact included within the case narrative. The project manager or appropriate technical personnel shall be notified as soon as possible to discuss possible corrective actions should unusually difficult sample matrices be encountered.*

I.11.4.1 Method blanks (MBs). These criteria shall be used to evaluate the acceptability of the MB data if project DQOs do not specify otherwise. The concentration of all target analytes shall be below one-half of the reporting limit (MRL) for each target analyte, or less than 5 percent of the regulatory limit associated with that analyte, or less than 5 percent of the sample result for the same analyte, whichever is greater for the MB to be acceptable. When this criterion is exceeded, corrective action should be taken to find/reduce/eliminate the source of this contamination in the MB. However, sample corrective action may be limited to qualification for blank contamination (i.e., B-flag). When the concentrations of any target analytes within the MB are above one-half the MRL for the majority of target analytes or above MRL for target analytes known to be common laboratory contaminants, assess the effect this may have had on the samples. If an analyte is found only in the MB, but not in any batch samples, no further corrective action may be necessary. Steps shall be taken to find/reduce/eliminate the source of this contamination in the MB. The case narrative should also discuss the situation. If an analyte is found in the MB and in some, or all, of the other batch samples, additional corrective action is required to reanalyze the MB, and any samples containing the same contaminant. If the contamination remains, the contaminated samples of the batch should be reprepared and reanalyzed with a new MB and batch-specific QC samples. Sporadic cases of contamination may be difficult to control; however, daily contamination would not be acceptable.

I.11.4.2 Laboratory control samples (LCSs). *The LCS is evaluated by comparing the percent recovery for all of the target analytes to the recovery measurement quality objectives as determined by project-specific DQOs, or the default ranges established in this guidance.* If target analytes are outside the acceptance windows, corrective action is required. Project DQOs will dictate the corrective actions necessary. Initially, the effect the QC failure has on the samples should be evaluated. Regardless of this assessment, steps shall be taken to find the source of the problem and correct it. The case narrative shall

discuss the corrective action taken and any other information. Typically, the LCS would be reanalyzed for the failed analytes only. If the second analysis fails, then the LCS, MB, and all associated samples of the batch would be reprepared and reanalyzed for the failed analytes only. *If sufficient sample is not available for repreparation and reanalysis or if the corrective action is ineffective, the sample results reported within that batch shall be flagged accordingly, and a discussion of the impact included within the case narrative.* When multiple (>5) target analytes are reported, the acceptance criteria may allow for the sporadic marginal failure of a few target analytes included within the LCS without requiring reanalysis of the entire batch. *For methods that report several (>5) target analytes, a small percentage of sporadic marginal failures may be tolerated (i.e., will not trigger reextraction and analysis of the entire batch). The number of target analytes reported for the method will dictate the number of allowable QC failures as given in table I-15.* Refer to the individual method tables (Tables I-1 through I-8) for details of this concept as it pertains to each of the methods discussed. The marginal failure allowance entails the application of an expanded acceptance criterion.

I.11.4.3 Matrix spike (MS) samples. *The MS is evaluated by comparing the recovery for target analytes to the recovery windows established within project documents, or those established in Tables I-1 through I-8.* MS data evaluation is more complex than MB or LCS data evaluation since MSs measure matrix effects in addition to sample preparation and analysis errors. The heterogeneity of soil, grab samples, and sequentially collected water samples further complicates the evaluation since matrix-specific bias assumes that the native concentrations in the duplicate analyses are constant. In addition concentrations of the target analytes in the sample can also far exceed the spike amounts added, making the resulting recoveries invalid. MSs that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. If the native concentration of target analytes in the sample chosen for spiking is high relative to the spiking concentration, the differences between the native concentration of the unspiked sample and the spiked samples may not be significant, making the bias measures unrepresentative of the true method and matrix performance. *For this reason, if the native concentration is two or more times the spiking level, corrective actions would be based on project DQOs.* Regardless, steps should be taken to find the cause of failure and corrective actions be taken to remedy it. If possible, respike the sample as outlined in the following sections at a higher level (e.g., at two to four times the sample concentration), then reanalyze the sample based on project-specific requirements. A review of the MSD result, if available, may confirm the matrix effect, if it is the same direction and same order of magnitude. If the native concentration is low, and the MS/MSD recoveries confirm matrix interference, reanalyze the MS/MSD sample/extract after employing cleanup procedures (organic analyses) or dilution techniques to minimize matrix interference. *If the matrix effect cannot be resolved, discuss the impact on the data within the case narrative.*

I.11.4.3.1   Inorganic analyses. Corrective action for unacceptable MS recoveries for ICP and GFAA analyses shall include implementation of a PDS from the same sample that the MS was prepared. In that way, information is obtained to identify whether matrix interference is occurring during the digestion or analytical procedures. Refer to Section I.11.4.6 for guidance on the evaluation of MS in conjunction with the PDS.

I.11.4.3.2   Organic analyses. When multiple (>5) target analytes are reported, the acceptance criteria may allow for the sporadic marginal failure of a few target analytes included within the MS without requiring reanalysis. When only a subset of target analytes is included in the MS, allow only one sporadic marginal failure. Reference Section I.9.3 and Tables I-1 through I-8 for information on the number of sporadic failures allowed and the expanded acceptance criteria to be applied.

I.11.4.4   Matrix duplicate (MD) and matrix spike duplicate (MSD) samples. The MSD is evaluated using the same bias criteria as described for the MS. *The MD or MSD is evaluated by comparing the*

precision for all target analytes to the windows as determined by project-specific DQOs, or as stated herein. These criteria should be applied only to concentrations of target analytes that are above the MQL of each analyte. MDs or MSDs that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. Corrective actions shall be performed as described for the MS.

I.11.4.5   Surrogates. *A surrogate is evaluated by comparing its recovery in each sample to the windows as determined by project-specific DQOs, or as stated within Tables I-3 through I-8*. Surrogate spikes in matrix-specific samples that fail to meet the appropriate acceptance criteria would indicate that a potential matrix effect is present. If significant nontarget interference occurs, corrective action shall include implementing additional cleanup procedures and reanalyses. *If this does not reduce the interference, discuss the impact on the data within the case narrative. Recommendations to the client may include method modifications, such as repreparation and reanalysis with smaller sample aliquots to reduce the effects of the matrix.* The consequences to detection limits must also be considered in this instance. Surrogate failures in MBs or LCSs are indicative of a general method failure and should be thoroughly investigated as noted in Sections I.11.4.1 and I.11.4.2, respectively.

I.11.4.6   Post-digestion spike samples. Default recovery control limits for the PDS are noted in Tables I-1 and I-2. Similar to the MS, if historic data or information on native sample concentrations is available, the MS or PDS should be spiked at a concentration at least twice the native sample concentration for the following evaluation to be considered valid. Professional judgment should be used to determine the corrective action necessary when the MS recovery for an analyte fails but the PDS recovery passes. *For instance, when the MS recovery fails because it falls below the lower control limit but the PDS recovery passes, confirmatory redigestion and reanalysis may not be required if allowed by project DQOs.* When both the MS and PDS indicate matrix interference is present, the laboratory must attempt to correct for the interference by the use of method of standard additions, an internal standard technique for ICP (e.g., with yttrium), a different matrix modifier for GFAA, or different digestion or analytical procedures to achieve a representative result, before qualifying the sample for matrix interference. This does not apply to sporadic failures but rather to target analytes exhibiting out-of-control recoveries on consecutive batches. Also, verify overall batch control for the analysis by evaluation of the LCS.

I.11.5   Calculation errors. Reports shall be reissued if calculation or reporting errors are noted with any given data package. The case narrative shall clearly state the reason(s) for reissuance of the report.

I.11.6   Onsite audits. A corrective actions report shall be required that addresses any deficiencies noted during audits conducted. *If corrective actions are needed for major deficiencies that would affect data quality, the laboratory should notify USACE of other projects that may be affected.*

I.12 Target Analyte Identification, Quantitation, and Confirmation

I.12.1 Target analyte identification.   Employ procedures presented within the individual determinative methods for determining presence and identification of target analytes within samples. *For GC/MS analyses and any samples containing extraneous peaks not associated with the calibration standards, a scan against a mass spectral library (typically ~75,000 compounds) may be performed for the purposes of tentative identification if warranted by project DQOs*. Based upon the degree of match, evidence of similar pattern, and analyst professional judgment, compounds may be reported as Tentatively Identified Compounds (TICs) and the analytical values estimated. *The necessity to perform this will depend on project-specific requirements. Recommend the use of TIC searches only in the early stages of site characterization on samples speculated as contaminated. Significant detections identified through TIC searches should require the inclusion of these compounds as project-specific target analytes. Future*

analyses shall require that calibration standards include these target analytes for more accurate quantitative determination of their result.

I.12.2   Target analyte quantitation. All samples shall be quantitated using the initial calibration curve, following procedures outlined within the determinative methods. Sample results that exceed the range of the initial calibration high standard must be diluted and reanalyzed, and sample analyte values reported below the MQL must be flagged as estimated quantities (i.e., J-flag). All dilutions must be applied to the sample results and reported accordingly. Solid samples are to be determined on a dry-weight basis. Sample target analyte values should be reported to three significant figures.

I.12.2.1   Inorganic analyses. Quantitative results are calculated using the mean value from the set of duplicate injections for Method 7010 or the mean value from multiple exposures for Method 6010. Also recommend the laboratory review the RPDs for duplicate injections/multiple exposures of samples exhibiting quantifiable concentrations. If the %RPD/%RSD is consistently >20 percent and highly variable for concentrations greater than the low-level calibration standard, corrective action should be taken. When matrix interference is suspected/confirmed, the use of method of standard additions must be used to calculate the sample result. The laboratory shall at a minimum use a series of three standard additions containing 50, 100, and 150 percent of the expected concentration. As outlined within the method, plot the absorbance of each solution at the concentration of the known standards. The concentration of the sample is then obtained from extrapolating the resulting line back to zero absorbance.

I.12.2.2   Organic analyses. The laboratory should make a reasonable attempt to correct for any matrix interference encountered. Dilutions should not be routinely used in preference to cleanup methods to address matrix interference. When matrix interference is present, samples should be processed using at least one cleanup method as outlined by the determinative method. Refer to Section I.6.8.2.2 for information on recommended cleanup methods. *If the cleanup and reanalysis do not reduce the matrix interference, discuss the impact on the data within the case narrative.*

I.12.2.2.1 Method 8081. In general, multiple-component analytes are quantitated (via external calibrations) by comparing the areas (or heights) for the characteristic peaks to the areas (or heights) for the corresponding calibration peaks of the same retention time and shape. Quantitation may be performed using a number (i.e., three to five) of major peaks or the total peak area of the appropriate pattern as described in the method. For chlordane, quantitate the peaks of alpha-chlordane, gamma-chlordane, and heptachlor separately against the initial 3-point calibration curves and report the individual results. When the GC pattern of the residue resembles that of technical chlordane, quantitate for this. Since commercial BHC (which consists of a mixture of six chemically distinct isomers and one or more heptachlorocyclohexanes and octachlorocyclohexanes) may exhibit a wide variance in the percentage of the individual isomers present, quantitate and report the alpha-, beta-, gamma-, and delta-BHC isomers separately. For DDT, the 4,4'-isomers of DDT, DDE, and DDD are the predominant pesticides in the environment and are the isomers normally regulated by USEPA. Therefore, quantitate separately and report the pure 4,4'-isomers of DDT.

I.12.2.2.2 Method 8330. Due to the lack of resolution between 2,4-DNT and 2,6-DNT, and between 2-Am-DNT and 4-Am-DNT, quantitation of these compounds may be expressed as isomeric pairs.

I.12.3   Target analyte confirmation. Chromatography is a technique that relies upon the comparison of retention times between standards and unknown peaks for qualitative identification. Unless mass spectrometry is used as the detector, tentative identification is based solely on the retention time of an unknown peak falling within the prescribed retention time window of a known standard. *In the absence of project-specific criteria, to minimize the possibility of incorrect identification (or false positives), confirmation*

shall be required for all chromatographic methods involving the analysis of single-component target analytes. Confirmation may be required for multicomponent analytes even though identification is achieved primarily through pattern recognition (i.e., PCBs, gasoline, etc.). For instance, PCB analysis requires second column confirmation when the Aroclor identification is in doubt, when a mixture of Aroclors are present, or when the pattern is weathered. It is recommended that confirmation techniques involve the use of another analytical technique (i.e., GC/MS), or a second dissimilar column. ***When project DQOs allow, a different type of detector may also be used.*** When the second dissimilar column is used, it shall be calibrated in the same manner as the primary column. After the target analyte has been identified, compare the primary and confirmatory results for agreement according to a method-prescribed criterion. Analytical results would normally be reported from the primary column unless interferences were noted. If quantitative results are reported from the confirmation column, the documentation from the analysis of all appropriate QC samples on the confirmation column shall also be required within the data package.

I.13 Data Reduction, Review, and Reporting

I.13.1   Data reduction. Data reduction procedures, whether performed by the instrument or manually, shall follow methodologies outlined within the laboratory SOP or analytical method. Project-specific variations of the general procedures, statistical approach, or formulas may be identified, depending on project-specific requirements. Automated procedures shall be verified as required by EPA's guidance on GALP (EPA 2185): all software shall be tested with a sample set of data to verify its correct operation via accurate capture, processing, manipulation, transfer, recording, and reporting of data.

I.13.2   Data review. All analytical data generated by the laboratory shall be extensively reviewed prior to report release to assure the validity of the reported data. This internal data evaluation process shall cover the areas of data generation, reduction, and a minimum three levels of documented review. For each level, the review process shall be documented using an appropriate checklist that is signed and dated by the reviewer. The analyst who generates the analytical data has the prime responsibility for the correctness and completeness of the data. Each step of this review process involves evaluation of data quality based on both the results of the QC data and the professional judgment of those conducting the review. This application of technical knowledge and experience to the data evaluation is essential in ensuring that data of known quality are generated consistently. All data generated and reduced shall follow well-documented in-house protocols.

I.13.2.1   Level 1 analyst review. Each analyst reviews the quality of his/her work based on an established set of guidelines. The review criteria as established in each method, in this guidance, or within the laboratory shall be used. This review shall, at a minimum, ensure the following:

- Sample preparation information is correct and complete.

- Analysis information is correct and complete.

- The appropriate SOPs have been followed.

- Analytical results are correct and complete.

- Raw data, including all manual integrations, have been correctly interpreted.

- QC samples are within established control limits.

- Special sample preparation and analytical requirements have been met.

- Data transfers were verified.

- Documentation is complete (e.g., all anomalies in the preparation and analysis have been documented, anomaly forms are complete, holding times are documented, etc.). Level 1 analyst review shall be documented by using a checklist and by the signature of the reviewer and date.

I.13.2.2   Level 2 peer review. Level 2 reviews shall be performed by a supervisor, another analyst, or data review specialist who has documentation that supports demonstration of performance for all areas for which he/she provides review. The function of this review is to provide an independent, complete peer review of the analytical batch data package. This review shall also be conducted according to an established set of guidelines and is structured to ensure the following:

- All appropriate laboratory SOPs have been referenced.

- Calibration data are scientifically sound, appropriate to the method, and completely documented.

- QC samples are within established guidelines.

- Qualitative identification of sample components is correct.

- Quantitative results, including calculations and any associated flags, are correct.

- Raw data, including manual integrations, have been correctly interpreted.

- Documentation is complete and correct (e.g., anomalies in the preparation and analysis have been documented, nonconformance forms are complete, holding times are documented, etc.).

- The data are ready for incorporation into the final report.

Level 2 reviews shall be structured so that all calibration data and QC sample results are reviewed and all of the analytical results are checked back to the raw data or bench sheets. If no problems are found with the data package, the review is complete. If any problems are found with the data package, then all sample results shall be returned to the analyst and rechecked. All errors and corrections noted shall be documented. Level 2 peer reviews shall also be documented on a checklist with the signature of the reviewer and date.

I.13.2.3   Level 3 administrative review. Level 3 reviews are performed by the program administrator or designee at the laboratory. This review shall provide a total overview of the data package, including sample receipt, to ensure its consistency and compliance with project-specific requirements. All errors noted shall be corrected and documented. Based on the errors noted, samples may need to be reprepared and reanalyzed. Level 3 administrative reviews shall also be documented on a checklist with the signature of the reviewer and date.

I.13.2.4   QA review. QA review is performed by the QA Officer or QA Branch. This review is not part of the normal production data review process. The QA Officer would typically review at least 10 percent of the data produced by the laboratory using the procedures as outlined in the Level 3 data reviews. Additional technical details should be reviewed in this QA review, similar to Levels 1 and 2, along

with a total package review, i.e., correlation of results from differing but related chemical parameters. The data packages reviewed would be randomly selected by the QA Officer. Nonconformance reports would be required for any errors noted.

I.13.3   Data qualifiers. Data qualifiers shall be added by the laboratory during the data generation/ review process. These qualifiers will be applied when measurement quality objectives defined in Section I.11 are not met and corrective action is not successful or when corrective action is not performed. All flags used by the laboratory shall be defined completely within the chemical data reportable packages. The following example data qualifiers are suggested for use:

- U = Nondetect when analyte concentration is below MRL.

- J = Estimated concentration when analyte concentration falls below the MQL (i.e., lowest calibration standard).

- B = Blank contamination when any associated blanks are above one-half the MRL.

- Q = Data requires usability review due to the exceedance of method-specific holding times, calibration, or batch QC data associated with the samples does not meet stated measurement quality objectives.

These flags should also identify any suspected bias in the data, either low or high, and whether the estimation is related to the suspected identification (qualitative) or whether the value reported is an approximation (quantitative). *The project manager or appropriate technical personnel shall be notified as soon as possible to discuss possible corrective actions should data be qualified. Additional data flagging may be performed by the USACE designee based upon overall project-specific requirements, through the use of external data review or validation.*

I.13.4   Data reporting requirements. The chemistry data package should contain enough information to demonstrate that the project data quality objectives have been fulfilled. In general, one should be able to determine the precision, bias, representativeness, comparability, and sensitivity of the data from information contained in the data package. This description applies to both primary and referee laboratory packages. The amount of information required to demonstrate attainment of DQOs depends upon the acceptable level of uncertainty for the intended data use. In general, the type of data package required will fall into one of four general categories: Screening, Definitive, Performance-Based, and Comprehensive. All reported data packages must be retained by the laboratory for a minimum of five (5) years, or as dictated by project requirements (if longer than five years). In the event of laboratory closure, all applicable documents must be transferred to the USACE client.

I.13.4.1   Screening data package. Screening data are generated by methods of analysis that tend to be relatively rapid, are performed in the field (as opposed to an offsite laboratory), and may have less rigorous sample preparation. Screening data provide analyte identification but may tend to report false positives. Their ability to quantitate analytes is in general less precise and less accurate than "definitive" type methods (see next section). Screening data must be confirmed by sending at least 10 percent of the samples for definitive analysis. The screening data package will depend on the screening method used. A typical screening data package will include the following:

- Sample identification number

- Preparation method

- Determinative method

- Detection limits

- Identity and quantity of analyte(s) present

- Date and time of sample collection

- Date of sample analysis

- Field equipment calibration

More sophisticated field screening methods will involve QC samples such as duplicate samples, calibration standards, spiked samples, or blank samples. Results for these associated QC samples should also be included in the screening data package.

I.13.4.2   Definitive data package. The definitive data package format allows for the review of the data by an independent organization. However, this data package does not allow for complete independent reconstruction of the analytical data. Definitive data are produced using rigorous analytical methods, such as USEPA standard reference methods (e.g., SW-846, CLP). Analyte presence and quantitation are confirmed through extensive quality control procedures at the laboratory, which may be onsite or offsite. As discussed in more detail in the following sections, the definitive data package should include a cover sheet, table of contents, case narrative, the analytical results, laboratory reporting limits, sample management records, and internal laboratory QA/QC information. The laboratory data package should be organized such that the analytical results are reported on a per-batch basis unless otherwise specified.

I.13.4.2.1 Cover sheet. The cover sheet should specify the following information:

- Title of report (i.e., Test Report, Test Certificate).

- Name and location of laboratory (to include a point of contact, phone and facsimile numbers).

- Name and location of any subcontractor laboratories, and appropriate test method performed.

- Contract number.

- Client name and address.

- Project name and site location.

- Statement of data authenticity and official signature and title of person authorizing report release.

- Amendments to previously released reports shall clearly identify the serial number for the previous report and state the reason(s) for reissuance of the report.

I.13.4.2.2 Table of contents. Laboratory data packages should be organized in a format that allows for easy identification and retrieval of information. An index or table of contents should be included for this purpose.

I.13.4.2.3 Case narrative. A case narrative should be included in each report. The case narrative should contain a table(s) summarizing samples received, providing a correlation between field sample numbers and laboratory sample numbers, and identifying which analytical test methods were performed and by which laboratories. Samples that were received but not analyzed should also be identified. Extractions or analyses that are performed out of holding times should be appropriately noted. The case narrative should define all data qualifiers or flags used. Deviations of any calibration standards or QC sample results from appropriate acceptance limits should be noted and associated corrective actions taken by the laboratory should be discussed. Any other factors that could affect the sample results (e.g., air bubbles in VOC sample vials, excess headspace in soil VOC containers, the presence of multiple phases, sample temperature and sample pH excursions, container type or volume, etc.) should be noted.

I.13.4.2.4 Analytical results. The results for each sample should contain the following information at a minimum. (Information need not be repeated if noted elsewhere in the data package).

- Laboratory name and location (city and state).

- Project name and unique ID number.

- Field sample ID number as written on custody form.

- Laboratory sample ID number.

- Matrix (soil, water, oil, etc.).

- Sample description.

- Sample preservation or condition at receipt.

- Date sample collected.

- Date sample received.

- Date sample extracted or prepared.

- Date sample analyzed.

- Analysis time when holding time limit <48 hours.

- Method (and SOP) numbers for all preparation, cleanup, and analysis procedures employed.

- Preparation, analysis, and other batch numbers.

- Analyte or parameter.

- Method reporting limits adjusted for sample-specific factors (e.g., aliquot size, dilution/ concentration factors, moisture content).

- Method quantitation limits (low-level standard concentration).

- Method detection limits.

- Analytical results with correct number of significant figures.

- All confirmation data.

- Any data qualifiers assigned.

- Concentration units.

- Dilution factors. All reported data shall reflect any dilutions or concentrations. The dilution factor, if applicable, should be noted on the analytical report. If neat and/or diluted results are available, data from all runs should be recorded and reported.

- Percent moisture or percent solids (all soils, sediments, sludges, etc. are to be reported on a dry weight basis).

- Chromatograms, as needed.

- Sample aliquot analyzed.

- Final extract volume.

I.13.4.2.5 Laboratory reporting limits. The laboratory may use a reporting limit expressed in terms of detection limit, quantitation limit, regulatory action level, or project-specific threshold limits. However, the laboratory's use of these terms must be well defined. In addition, the "<" reporting convention must be used in accordance with the requirements established in Section I.3.3.7.3.

I.13.4.2.6 Sample management records. These types of records include the documentation accompanying the samples (i.e., original chain-of-custody record, shipping documents, laboratory notification sheets), records generated by the laboratory that detail the condition of the samples upon receipt at the laboratory (i.e., sample cooler receipt forms, any telephone conversation records, etc.), and any records generated to document sample custody, transfer, analysis, and disposal.

I.13.4.2.7 QA/QC information. The minimum data package must include the calibration, calibration verification, and internal laboratory QA/QC data with their respective acceptance criteria. The data package should also include the laboratory's method quantitation and reporting limits for project-specific parameters. The calibration data shall include a summary of the ICV, all calibration verification standards, and any performance standards analyzed in conjunction with the test method. All calibration deviations shall be discussed within the case narrative. The data package should correlate the method QC data with the corresponding environmental samples on a per-preparation batch basis with batch numbers clearly shown. Method QC data must include all spike target concentration levels; the measured spike concentration and calculated recoveries; all measures of precision, including relative percent difference; and all control limits for bias and precision. This would include laboratory performance information such as results for MBs, recoveries for LCSs, and recoveries for QC sample surrogates; and matrix-specific information such as MD RPDs, MS and MSD recoveries, MS/MSD RPDs, field sample surrogate recoveries, SDs, and PDS, etc. At a minimum, internal QC samples should be analyzed and reported at rates specified in the specific methods, within USACE guidance, or as specified in the contract, whichever is greater. Any deviations from the measurement quality objectives should be noted. Also include any data review, nonconformance, or corrective action forms within the data package.

I.13.4.3 Performance-based data package. The requirements for the ***performance-based data package are the same as those defined within the definitive data package with the addition of the following items: all appropriate project action level(s) and DQOs and appropriate preparatory and analysis logs.***

I.13.4.4   Comprehensive data package.   A comprehensive data package contains sufficient information to completely reconstruct the chemical analyses that were performed. Hence, comprehensive data packages include all batch QC results, instrument QC results (e.g., initial calibration verification, continuing calibration verification, and instrument performance checks), MDL studies, and raw data (e.g., run logs, sample preparation logs, standard preparation logs, and printed instrumental output such as chromatograms). Typically, comprehensive data packages are required if third-party data validation is to be performed. The data validation guidelines for performance-based methods established in other USACE guidance on data review and data validation, USEPA national functional guidelines, USEPA regional functional guidelines, and project-specific guidelines for validation may all have distinct reporting formats. The appropriate validation guidelines should be consulted to determine what type of data package is required.

I.13.4.5   Chemistry data package deliverable time schedule. A schedule for data delivery should be established so that data packages are provided as needed for chemical QA assessment. This includes identifying the anticipated number or frequency of these data packages in light of project objectives, i.e., the amount of data produced or project duration.

I.13.4.6   Electronic data deliverables. Electronic data deliverables (EDDs) may be specified either in addition to or in lieu of hard copy requirements. EDDs shall contain the same information as described for the hard copy deliverables. The complete set of rules for representing these data in a form suitable for transmission is called an EDD format. EDDs should use a common syntax for terms used to describe diverse laboratory activities and report analytical data. EDDs should also provide sufficient input parameters to allow users to link analytical data to underlying laboratory activities, full traceability for data, and a means for reporting complex analytical relationships. Examples of EDDs include DEEMS, IRPMIS, COELT, etc. DEEMS (Department of Energy Environmental Management Electronic Data Deliverable Master Specification) is based on a sophisticated model of analytical activities and uses a flexible way of representing the linkages between these activities. DEEMS is the recommended EDD for USACE projects when electronic data are specified. Information on the availability of this DEEMS implementation guide may be obtained from the Chemical Data Quality Management Branch, Hazardous, Toxic, and Radioactive Waste Center of Expertise, U.S. Army Corps of Engineers.

Table I-1
Summary of Measurement quality objectives for Method 6010 Inductively Coupled Plasma (ICP) Metals

Quality Control Element	Description of Element	Frequency of Implementation	Acceptance Criteria
Initial Calibration (I.9.2.1.1)	Option 1- 1 std and blank, and a low-level check standard at MQL Option 2- 3 stds and blank	Daily	Option 1- Low-level check standard ± 20% Option 2- r $ 0.995
Instrumental Precision (I.9.2.1.1)	%RSD 3 integrations (exposures)	Each calibration and calibration verification standards (ICV/CCV)	%RSD < 5%
Initial Calibration Verification (ICV) (I.9.3)	Midlevel (2nd source) verification	After initial calibration	%Recovery ± 10%
Initial Calibration Blank (ICB) (I.9.4)	Interference-free matrix to assess analysis contamination	After initial calibration	Analytes < MDL
Interelement Check Standards (ICS) (I.8.1)	ICS-A - interferents only ICS-B - interferents and target analytes	Beginning of analytical sequence	%Recovery ± 20% for target analytes
Continuing Calibration Blank (CCB) (I.9.4)	Interference-free matrix to assess analysis contamination	Every 10 samples and at end of analytical sequence	Analytes < MDL
Continuing Calibration Verification (CCV) (I.9.5 / I.9.5.1)	Midlevel verification	Every 10 samples and at end of analytical sequence	%Recovery ± 10%
Method Blank (MB) (I.10.2.1 / I.11.4.1)	Interference-free matrix to assess overall method contamination	1 per sample batch	Analytes < one-half MRL
Laboratory Control Sample (LCS) (I.10.2.2 / I.11.4.2)	Interference-free matrix containing all target analytes	1 per sample batch	%Rec = 80% - 120% Sporadic marginal failures[1]: %Rec = 60% - 140%
Matrix Spike (MS) (I.10.2.3 / I.11.4.3 / I.11.4.3.1)	Sample matrix spiked with all/subset of target analytes prior to digestion	1 per sample batch	%Rec = 75% - 125%
Matrix Duplicate (MD) or Matrix Spike Duplicate (MSD) (I.10.2.4 / I.11.4.4)	Refer to text for MD or MS.	1 per sample batch	RPD # 25%
Post Digestion Spike (PDS) (I.10.3.1 / I.11.4.6)	Sample digestate spiked with all/subset of target analytes	1 per sample batch on MS sample	%Rec = 75% - 125%
Serial Dilution (SD) (I.10.3.2)	1:4 dilution analyzed to assess matrix effects	As needed to assess new and unusual matrices	Agreement between undiluted and diluted results ± 10%
Method of Standard Additions (MSA) (I.12.2.1)	Method of quantitation	As needed for samples with suspected or confirmed matrix effects	r $ 0.995

[1] The number of Sporadic Marginal Failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if between 7 to 15 metals are reported from the ICP analysis, one (1) SMF is allowed to the expanded criteria presented. If greater than 15 metals are reported from the ICP analysis, two (2) SMFs are allowed.

Table I-2
Summary of Measurement quality objectives for Method 7010/7470/7471 Series GFAA/CVAA Metals

Quality Control Element	Description of Element	Frequency of Implementation	Acceptance Criteria
Initial Calibration (I.9.2.1.2)	3 stds and blank(GFAA) 5 stds and blank(CVAA)	Daily	r $ 0.995
Instrumental Precision (I.9.2.1.2)	RPD of 2 injections	All standards, and ICV/CCV	RPD ± 10%
Initial Calibration Verification (ICV) (I.9.3)	Midlevel (2nd source) verification	After initial calibration	%Rec ± 10%
Initial Calibration Blank (ICB) (I.9.4)	Interference-free matrix to assess analysis contamination	After initial calibration	Analytes < MDL
Continuing Calibration Blank (CCB) (I.9.4)	Interference-free matrix to assess analysis contamination	Every 10 samples and at end of analytical sequence	Analytes < MDL
Continuing Calibration Verification (CCV) (I.9.5 / I.9.5.1)	Midlevel verification	Every 10 samples and at end of analytical sequence	%Rec ± 20%
Method Blank (MB) (I.10.2.1 / I.11.4.1)	Interference-free matrix to assess overall method contamination	1 per sample batch	Analytes < one-half MRL
Laboratory Control Sample (LCS) (I.10.2.2 / I.11.4.2)	Interference-free matrix containing target analytes	1 per sample batch	%Rec = 80% - 120%
Matrix Spike (MS) (I.10.2.3 / I.11.4.3 / I.11.4.3.1)	Sample matrix spiked with target analytes prior to digestion	1 per sample batch	%Rec = 80% - 120%
Matrix Duplicate (MD) or Matrix Spike Duplicate (MSD) (I.10.2.4 / I.11.4.4)	Refer to text for MD or MS.	1 per sample batch	RPD # 20%
Post Digestion Spike (PDS) (I.10.3.1 / I.11.4.6)	Sample digestate spiked with target analytes	Every sample	%Rec = 85% - 115%
Serial Dilution (SD) (I.10.3.2)	1:4 dilution analyzed to assess matrix effects	As needed to assess new and unusual matrices	Agreement between undiluted and diluted results ± 10%
Method of Standard Additions (MSA) (I.12.2.1)	Method of quantitation	As needed for samples with suspected or confirmed matrix effects	r $ 0.995

Note: GFAA = Graphite furnace - atomic absorption spectroscopy.
    CVAA = Cold vapor - atomic absorption.

Table I-3
Summary of Measurement quality objectives for Method 8021 VOCs

QC Element	Target Analyte/Surrogate	Poor Purgers/Gases/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.1)	Primary Evaluation: r $ 0.995, %RSD # 20%, r^2 $ 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes # 20%	Alternative Evaluation: Maximum allowable %RSD for each target analyte # 40%
ICV (I.9.3)	%Rec = 85% - 115%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9.5.2.1)	Primary Evaluation: %Drift # 15%, %D # 15%	Primary Evaluation: %Drift # 20%, %D # 20%
	Alternative Evaluation: Mean %Drift/%D for all target analytes # 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analytes # 30%
MB (I.10.2.1 / I.11.4.1)	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	%Rec = 70% - 130%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MSD/MD (I.10.2.4 / I.11.4.4)	Water: RPD # 30% Solids: No RPD Limits	Water: RPD # 40% Solids: No RPD Limits
Surrogates (I.10.2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125% Project Sample Matrix: %Rec = 70% - 130%	Not applicable
Target Analyte Confirmation (I.12.3)	RPD # 40%	RPD # 40%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the 8020 Target Analyte List (10 compounds) is reported, 1 SMF is allowed. If the 8010 Target Analyte List (32 compounds) is reported, 3 SMFs are allowed. If the full 8021 Target Analyte List (60 compounds) is reported, 4 SMFs are allowed. If the MS includes only a subset of compounds, allow only 1 SMF for that QC element..

Table I-4
Summary of Measurement quality objectives for Method 8081 Pesticides

QC Element	Target Analyte/Surrogate	Sporadic Marginal Failure [1]
DDT/Endrin %Breakdown (I.8.2)	DDT & Endrin %Breakdown # 15% each	Not Applicable
Initial Calibration (I.9.2.2.4)	Primary Evaluation: r $ 0.995, %RSD # 20%, r^2 $ 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes # 20%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte # 40%
ICV (I.9.3 / I.9.3.1)	%Rec = 85% - 115%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9.5.2.2)	Primary Evaluation: %Drift # 15%, %D # 15%	No allowance
	Alternative Evaluation: Mean %Drift/%D for all target analytes # 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analyte # 30%
MB (I.10.2.1 / I.11.4.1)	Analytes < one-half MRL	Not applicable
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130%	Sporadic Marginal Failures[1]: %Rec = 30% - 150%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	%Rec = 40% - 140%	Sporadic Marginal Failures[1]: %Rec = 30% - 150%
MSD/MD (I.10.2.4 / I.11.4.4)	RPD # 50%	RPD # 60%
Surrogates (I.10.2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130% Project Sample Matrix: %Rec = 40% - 140%	Not applicable
Target Analyte Confirmation (I.12.3)	RPD # 40%	RPD # 40%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the full list of 21 compounds is reported from the GC/electron capture detector analysis, then 2 SMFs are allowed to the expanded criteria presented. If the MS includes only a subset of compounds, allow only 1 SMF for that QC element.

Table I-5
Summary of Measurement quality objectives for Method 8082
PCBs

QC Element	Target Analyte/Surrogate
Initial Calibration (I.9.2.2.5)	r $ 0.995, RSD # 20%, r^2 $ 0.990
ICV (I.9.3 / I.9.3.2)	%Rec = 85% - 115%
CCV (I.9.5 / I.9.5.2)	%Drift # 15%, %D # 15%
MB (I.10.2.1 / I.11.4.1)	Analytes < one-half MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130%
MS (I.10.2.3 / I.11.4.3)	%Rec = 40% - 140%
MSD/MD (I.10.2.4 / I.11.4.4)	RPD = 50%
Surrogates (I.10.2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 50% - 130% Solids: %Rec = 50% - 130% Project Sample Matrix: %Rec = 40% - 140%
Target Analyte Confirmation (I.12.3)	RPD # 40%

Table I-6
Summary of Measurement quality objectives for Method 8260 VOCs

QC Element	Target Analyte/Surrogate	Poor Purgers/Gases/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.4)	Instrument Evaluation: System performance check compounds (SPCCs): minimum response factor (RF) values per method requirements Calibration check compounds (CCCs): verify %RSD # 30%	No allowance
	Primary Evaluation: r $ 0.995, %RSD # 15%, r^2 $ 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes # 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte # 30%
ICV (I.9.3)	%Rec = 80% - 120%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9.5.2.4)	Instrument Evaluation: SPCCs: minimum RF values per method requirements	No allowance
	Primary Evaluation (CCCs): %Drift # 20%, %D # 20%	No allowance
MB (I.10.2.1 / I.11.4.1)	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	%Rec = 70% - 130%	Sporadic Marginal Failures[1]: %Rec = 60% - 140%
MSD/MD (I.10.2.4 / I.11.4.4)	Water: RPD # 30% Solids: No RPD Limits	Water: RPD # 40% Solids: No RPD Limits
Surrogates (I.10.2.5 / I.11.4.5)	%Interference-Free Matrix: Water: %Rec = 80% - 120% Solids: %Rec = 75% - 125% Project Sample Matrix: %Rec = 70% - 130%	Not applicable

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the full list of 68 compounds is reported from the GC/MS analysis, then 5 SMFs are allowed to the expanded criteria presented for the LCS. If the MS includes only a subset of compounds, allow only 1 SMF for this QC element.

Table I-7
Summary of Measurement quality objectives for Method 8270 Semivolatiles

QC Element	Target Analyte/Surrogate	Poor Performers/Sporadic Marginal Failures[1]
Initial Calibration (I.9.2.2.7)	Instrument Evaluation: SPCCs: minimum RF values per method requirements CCCs: verify %RSD # 30%	No allowance
	Primary Evaluation (all target analytes) : r $ 0.995, %RSD # 15%, r² $ 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes # 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte # 40%
ICV (I.9.3)	%Rec = 70% - 130%	No allowance
CCV (I.9.5 / I.9.5.2 / I.9.5.2.4)	Instrument Evaluation: SPCCs: minimum RF values per method requirements	No allowance
	Primary Evaluation (CCCs): %Drift # 20%, %D # 20%	No allowance
MB (I.10.2.1 / I.11.4.1)	Target Analytes: Analytes < one-half MRL	Common Lab Contaminants: Analytes < MRL
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 60% - 120% (~15 analytes) = 45% - 135% (~30 analytes) = 20% - 150% (~15 analytes) Solids: %Rec = 60% - 120% (~20 analytes) = 45% - 135% (~25 analytes) = 30% - 150% (~15 analytes)	Sporadic Marginal Failures[1]: Water: %Rec = 15% - 150% Solids: %Rec = 25% - 150%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	Water: %Rec = 45% - 135% Solids: %Rec = 45% - 135%	Sporadic Marginal Failures[1]: Water: %Rec = 15% - 150% Solids: %Rec = 20% - 150%
MSD/MD (I.10.2.4 / I.11.4.4)	Water: RPD # 50% Solids: RPD # 60%	Sporadic Marginal Failures[1]: Water: RPD # 60% Solids: RPD # 60%
Surrogates (I.10.2.5 / I.11.4.5)	%Interference-Free Matrix[2]: Water: %Rec = 60% - 120% B/N cmpds %Rec = 45% - 135% A cmpds Solids: %Rec = 60% - 120% B/N cmpds %Rec = 45% - 135% A cmpds Project Sample Matrix:[2] Water: %Rec = 45% - 135% B/N cmpds %Rec = 35% - 140% A cmpds Solids: %Rec = 45% - 135% B/N cmpds %Rec = 35% - 140% A cmpds	Sporadic Marginal Failures[1]: Water: %Rec = 15% - 150% Solids: %Rec = 20% - 150%

[1] The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if the full list of target compounds as presented in Table 13 are reported, then 5 SMFs are allowed to the expanded criteria presented for the LCS. If the MS includes only a subset of compounds and for Surrogates, allow up to 1 SMF.
[2] B = base, N = neutral, and A = acid compounds (cmpds).

Table I-8
Summary of measurement quality objectives for Method 8330 Explosives

Initial Calibration (I.9.2.2.8)	Primary Evaluation: r $ 0.995, RSD # 20%, r^2 $ 0.990	No allowance
	Alternative Evaluation: Mean %RSD for all target analytes # 20%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %RSD for each individual target analyte # 40%
ICV (I.9.3)	%Rec = 85% - 115%	No allowance
CCV (I.9.5 / I.9.5.2)	Primary Evaluation: %Drift # 15%, %D # 15%	No allowance
	Alternative Evaluation: Mean %Drift/%D for all target analytes # 15%, with maximum allowable restriction noted at right for individual analytes.	Alternative Evaluation: Maximum allowable %Drift/%D for each individual target analyte # 30%
MB (I.10.2.1 / I.11.4.1)	Target Analytes: Analytes < one-half MRL	Not applicable
LCS (I.10.2.2 / I.11.4.2)	Water: %Rec = 60% - 120%[2] Solids: %Rec = 60% - 120%[2]	Sporadic Marginal Failures[1]: %Rec = 40% - 150%
MS (I.10.2.3 / I.11.4.3 / I.11.4.3.2)	%Rec = 50% - 140%[2]	Sporadic Marginal Failures[1]: %Rec = 40% - 150%
MSD/MD (I.10.2.4 / I.11.4.4)	RPD # 50%	RPD # 60%
Surrogates (I.10.2.5 / I.11.4.5)	Interference-Free Matrix: Water: %Rec = 60% - 140% Solids: %Rec = 50% - 150% Project Sample Matrix: %Rec = 50% - 150%	Not applicable
Target Analyte Confirmation (I.12.3)	RPD # 40%	RPD # 40%

[1]   The number of sporadic marginal failure (SMF) allowances depends upon the number of target analytes reported from the analysis. For instance, if between 7 to 15 explosives are reported from the high-performance liquid chromatography analysis, 1 SMF is allowed to the expanded criteria presented for the LCS. If greater than 15 explosives are reported, 2 SMFs are allowed for the LCS. If the MS includes only a subset of compounds, allow only 1 SMF for this QC element.
[2]   Due to the tendency for Tetryl to decompose, an expanded criteria may be applied at 45% - 140% for both water and soil matrices.

Table I-9
Target Analyte List for Method 8021 VOCs

Target Analyte	Chemical Abstract Service (CAS) Registry No.
Benzene [1, 2]	71-43-2
Bromobenzene [3]	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane [3]	75-27-4
Bromoform [3]	75-25-2
Bromomethane [3, 4]	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride [3]	56-23-5
Chlorobenzene [1, 3]	108-90-7
Chloroethane [3, 4]	75-00-3
Chloroform [3]	67-66-3
Chloromethane [3, 4]	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane [3]	124-48-1
1,2-Dibromo-3-chloropropane [5]	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane [3]	74-95-3
1,2-Dichlorobenzene [1, 3]	95-50-1
1,3-Dichlorobenzene [1, 3]	541-73-1
1,4-Dichlorobenzene [1, 3]	106-46-7
Dichlorodifluoromethane [3, 4]	75-71-8
1,1-Dichloroethane [3]	75-34-3
1,2-Dichloroethane [3]	107-06-2
1,1-Dichloroethene [3]	75-35-4
cis-1,2-Dichloroethene	156-59-2

(Continued)

[1]   AVO target analytes.
[2]   BTEX target analyte list.
[3]   HVO target analytes.
[4]   Gaseous target analyte.
[5]   Exhibits poor purging efficiency or instrumental response.

Table I-9 (Concluded)

Target Analyte	CAS Registry No.
trans-1,2-Dichloroethene [3]	156-60-5
1,2-Dichloropropane [3]	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene [3]	10061-01-5
trans-1,3-Dichloropropene [3]	10061-02-6
Ethyl Benzene [1,2]	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene (Cumene)	98-82-8
p-Isoproplytoluene (p-Cumene)	99-87-6
Methylene chloride [3]	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane [3]	630-20-6
1,1,2,2-Tetrachloroethane [3]	79-34-5
Tetrachloroethene [3]	127-18-4
Toluene [1,2]	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane [3]	71-55-6
1,1,2-Trichloroethane [3]	79-00-5
Trichloroethene (trichloroethylene) [3]	79-01-6
Trichlorofluoromethane [3,4]	75-69-4
1,2,3-Trichloropropane [3]	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride [3,4]	75-01-4
o-Xylene [1,2]	95-47-6
m-Xylene [1,2]	108-38-3
p-Xylene [1,2]	106-42-3

[1]   AVO target analytes.
[2]   BTEX target analyte list.
[3]   HVO target analytes.
[4]   Gaseous target analyte.

Table I-10
Target Analyte List For Method 8081 Pesticides

Target Analyte	CAS Registry No.
Aldrin	309-00-2
alpha-BHC	319-84-6
beta-BHC	319-85-7
gamma-BHC (Lindane)	58-89-9
delta-BHC	319-86-8
alpha-Chlordane	5103-71-9
gamma-Chlordane	5103-74-2
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Methoxychlor	72-43-5
Toxaphene	8001-35-2

Table I-11
Target Analyte List for Method 8082 PCBs

Target Analyte	CAS Registry No.
As Aroclors	
Aroclor-1016	12674-11-2
Aroclor-1221	11104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5
Congeners	
2-Chlorobiphenyl	2051-60-7
2,3-Dichlorobiphenyl	16605-91-7
2,2',5-Trichlorobiphenyl	37680-65-2
2,4',5-Trichlorobiphenyl	16606-02-3
2,2',3,5'-Tetrachlorobiphenyl	41464-39-5
2,2',5,5'-Tetrachlorobiphenyl	35693-99-3
2,3',4,4'-Tetrachlorobiphenyl	32598-10-0
2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8
2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2
2,3,3',4',6-Pentachlorobiphenyl	38380-03-9
2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2
2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6
2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5
2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1
2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6
2,2',3,4,4',5, 5'-Heptachlorobiphenyl	35065-29-3
2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1
2,2',3,4,5,5',6-Heptachlorobiphenyl	52663-68-0
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9

Table I-12
Target Analyte List for Method 8260 VOCs

Target Analyte	CAS Registry No.
Acetone [1]	67-64-1
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane [1]	74-83-9
2-Butanone (methyl ethyl ketone) [1]	78-93-3
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon disulfide [1]	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane [1]	75-00-3
Chloroform	67-66-3
Chloromethane [1]	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane [1]	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane [1]	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-59-2
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6

(Continued)

[1] Denotes poor purging efficiency or poor response.

Table I-12 (Concluded)

Target Analyte	CAS Registry No.
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethyl Benzene	100-41-4
Hexachlorobutadiene	87-68-3
2-Hexanone [1]	591-78-6
Iodomethane	74-88-4
Isoproplybenzene (Cumene)	98-82-8
p-Isoproplytoluene (p-Cumene)	99-87-6
Methylene chloride	75-09-2
4-Methyl-2-pentanone [1]	108-10-1
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene (trichloroethylene)	79-01-6
Trichlorofluoromethane [1]	75-69-4
1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride [1,2]	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

[1] Denotes poor purging efficiency or poor response.
[2] Gaseous target analyte.

Table I-13
Target Analyte List For Method 8270

Target Analyte	CAS Registry No.
Base/Neutral Fraction	
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
Aniline [1]	62-53-3
Anthracene	120-12-7
Benzidine [1]	92-87-5
Benzo(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo(a)pyrene	50-32-8
Benzyl alcohol [1]	100-51-6
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
4-Chloroaniline [1]	106-47-8
bis(2-Chloroethoxy)methane	111-91-1
bis(2-Chloroethyl) ether	111-44-4
bis(2-Chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Di-n-butyl phthalate	84-74-2
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
3,3'-Dichlorobenzidine	91-94-1
Diethyl phthalate [1]	84-66-2
Dimethyl phthalate	131-11-3

[1]   Denotes poor extraction efficiency, tendency to decompose, or poor chromatographic behavior.

(Sheet 1 of 3)

Table I-13 (Continued)

Target Analyte	CAS Registry No.
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Di-n-octyl phthalate	117-84-0
Diphenyl amine	122-39-4
1,2-Diphenylhydrazine	122-66-7
bis(2-Ethylhexyl) phthalate	117-81-7
Fluoranthene	206-44-0
Fluorene	86-73-7
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene [1]	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isophorone	78-59-1
2-Methylnaphthalene	91-57-6
Naphthalene	91-20-3
2-Naphthylamine	91-59-8
2-Nitroaniline [1]	88-74-4
3-Nitroaniline [1]	99-09-2
4-Nitroaniline [1]	100-01-6
Nitrobenzene	98-95-3
N-Nitroso-dimethylamine [1]	62-75-9
N-Nitrosodiphenylamine [1,2]	86-30-6
N-Nitroso-di-n-propylamine	621-64-7
N-Nitrosopyrrolidine	930-55-2
Phenanthrene	85-01-8
Pyrene	129-00-0
Pyridine	110-86-1
1,2,4,5-tetrachlorobenzene	95-94-3
1,2,4-Trichlorobenzene	120-82-1

[1] Denotes poor extraction efficiency, tendency to decompose, or poor chromatographic behavior.
[2] N-Nitrosodiphenylamine coelutes with and cannot be differentiated from diphenylamine.

(Sheet 2 of 3)

Table I-13 (Concluded)
Acid Fraction Target Analyte List For Method 8270

Target Analyte	CAS Registry No.
Acid Fraction	
Benzoic Acid [1]	65-85-0
4-Chloro-3-methylphenol [1]	59-50-7
2-Chlorophenol	95-57-8
2,4-Dichlorophenol	120-83-2
2,6-Dichlorophenol	87-65-0
2,4-Dimethylphenol [1]	105-67-9
4,6-Dinitro-2-methylphenol [1]	534-52-1
2,4-Dinitrophenol [1]	51-28-5
2-Methylphenol [1] (o-cresol)	95-48-7
3-Methylphenol [1,3] (m-cresol) & 4-Methylphenol [1,3] (p-cresol)	108-39-4 & 106-44-5
2-Nitrophenol [1]	88-75-5
4-Nitrophenol [1]	100-02-7
Pentachlorophenol [1]	87-86-5
Phenol [1]	108-95-2
2,4,5-Trichlorophenol	95-95-4
2,4,6-Trichlorophenol	88-06-2

[1]   Denotes poor extraction efficiency, tendency to decompose, or poor chromatographic behavior.
[3]   3-Methylphenol (m-cresol) coelutes with 4-Methylphenol (p-cresol). Therefore, both are reported as isomeric pairs.

(Sheet 3 of 3)

Table I-14
Target Analytes For Method 8330 Explosives

Target Analyte	CAS Registry No.
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	121-82-4
1,3,5-Trinitrobenzene (1,3,5-TNB)	99-35-4
1,3-Dinitrobenzene (1,3-DNB)	99-65-0
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	479-45-8
Nitrobenzene (NB)	98-95-3
2,4,6-Trinitrotoluene (2,4,6-TNT)	118-96-7
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	1946-51-0
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	355-72-78-2
2,4-Dinitrotoluene (2,4-DNT)	121-14-2
2,6-Dinitrotoluene (2,6-DNT)	606-20-2
2-Nitrotoluene (2-NT)	88-72-2
3-Nitrotoluene (3-NT)	99-08-1
4-Nitrotoluene (4-NT)	99-99-0

Table I-15
Number of Allowable QC Failures

N	X
5 - 15	1
16 - 30	2
31 - 45	3
46 - 60	4
61 - 75	5
76 - 90	6
91 - 105	7

Note: N = number of reported method target analytes
    X = sporadic marginal failures allowed